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ULTRAMICROSCOPIC INVESTIGATION OF THE ELECTROLYSIS OF SOLUTIONS OF SILVER NITRATE

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Considerable attention has been devoted to the problem of the electrocrystallization of metals in electrochemical literature; this may be explained by the fact that the reason for the obtaining of one quality of metal or another is usually considered to be the electrolysis conditions, on which the final stage of the cathode process largely depends -- the crystallization of the metal from its atoms formed as the ions are discharged.

In particular, many of the papers in this field deal with the electrocrystallization of silver during the electrolysis of solutions of its salts.

Among the earliest of such papers are the rather extensive researches of Kohlschutter [1]. In his papers, containing experimental confirmation, the author points out the feasibility of the formation of colloidal systems during electrolysis and, examining colloidal solutions of silver, considers them to be an intermediate phase of the separation of silver at the cathode.

The constitution of colloidal systems during the electrolysis of silver-nitrate solutions had also been observed by other researchers. Thus, Kosonogov [2], observing the electrolysis of N/100 solutions under the ultramicroscope, discovered the formation of numerous mobile particles in the layer of the electrolyte near the cathode. To judge from the author's description of what he had seen, it may be concluded that what he observed was the formation of colloidal systems during electrolysis, though the author himself came to no such conclusion.

Systems of this sort were likewise obtained by Vozvizhensky [3] during the electrolysis of silver nitrate solutions; he called them thin suspensions, though in another paper [4] reporting on observations of the electrolysis of these solutions under the ultramicroscope, he speaks of observing vigorous Brownian movement of the particles formed.

Pavlov [5] and Zaprometov [6] likewise speak of the formation of colloidal systems in the electrolysis of silver-nitrate solutions. Thus, there apparently can be no doubt of the formation of colloidal systems in the electrolysis of silver-nitrate solutions. But it must be remembered that the problem of whether colloidal particles are formed at the cathode under all conditions of electrolysis or only under some conditions, and if so, under what conditions, is not entirely clear.

Another question, of fundamental importance but still moot, is the nature of the colloidal particles formed during electrolysis.

In his research, Vozdvizhensky endeavored to establish the nature of these particles experimentally, coming to the conclusion that in the electrolysis of silver-nitrate solutions what are formed are thin suspensions of silver hydroxide, rather than colloidal metal. The author based his conclusions upon the observed dissolution of the ''suspended matter'' when it came in contact with anode products and when more acid was added, as well as upon the ultramicroscopic picture observed by him in the electrolysis of acid solutions and the external analogy of the phenomena observed during electrolysis with what occurs when an alkaline solution is added to solutions of silver nitrate.

If the research methods employed by the author are borne in mind, the conclusions he drew on the basis of these three arguments is open to question.

The author performed his experiments under conditions that did not exclude the access of air and the liberation of oxygen at the platinum anodes; but it is known that silver is not stable under the action of acid solutions, including those of organic acids, when oxygen is allowed to have access to the metal [7]. All the more is this so in the case of colloidal silver, when it is in the state of a high degree of disintegration.

Some doubt is also aroused by the author's extremely brief periods of ultramicroscopic observation (1 to 20 seconds).

The analogy mentioned can hardly serve as an indication of the correctness of the conclusion made by the author.

What is of fundamental importance, but has not been elucidated experimentally in the literature, is the question of the fate of the colloidal particles formed during electrolysis, and more particularly, the question of whether the colloidal particles take a direct part in building up the cathode deposit.

We established the existence of such a phenomenon -- the participation of the colloidal particles formed during electrolysis in building up the deposit of metal on the cathode -- visually [8], in our investigations of the electrolysis of copper-sulfate solutions under the ultramicroscope.

The object of the researches listed below was to arrive at a solution of the indicated questions on the basis of the results of the research.

EXPERIMENTAL

The instrument used in our research was an ultramicroscope. The method of research was analogous to that employed by us earlier [8]. The electrodes were made of silver wire 1.0 mm in diameter.

The use of silver electrodes involved a considerable advantage over that of platinum ones, since it enabled us to carry out the electrolysis without liberating oxygen at the anode, afforded an adequate guarantee against changes in the composition of the electrolyte, and eliminated a cathode that was not identical with the metal separated at it. The electrodes were placed 5 mm apart in the electrolytic cell (chamber). The surface of the electrode traversed by the current was 25-30 sq. mm. All observations were carried out at a temperature of 18-20°. Silver nitrate solutions ranging from N/10,000 to N/10 were used in the experiments.

At first, the ultramicroscopic observations were made with solutions prepared in dark-red light in quartz vessels, using distilled water, which had been distilled in quartz apparatus and collected in a quartz receiver. Solutions prepared in this manner proved to be optically inactive media.

It was subsequently found that solutions made under electric light, in glass vessels, with ordinary, freshly distilled water that was not exposed to daylight, also proved to be adequately optically inactive media; under identical conditions, the observed results of the electrolysis of these solutions did not differ from the observed results of the electrolysis of solutions prepared with the precautions stated above. For that reason, many of the observations whose results are listed below were made with such solutions, which were employed in the experiments immediately after being prepared.

Two series of tests were made. One series was made with pure solutions of silver nitrate. In the other series of tests the same solutions were used with the addition of acids, chiefly nitric acid.

Test Results

The ultramicroscopic picture was sufficiently uniform in the electrolysis of neutral solutions of all the concentrations listed above, up to bath voltages of 0.9 - 1.1 volts.

The uninterrupted formation of colloidal particles about the cathode was established visually. They increased in quantity as the current rose and as the solution concentration diminished. Depending on these electrolysis conditions, the number of particles that made their appearance at the cathode per second ranged from $4 \cdot 10^3$ to $60 \cdot 10^3$ per sq mm of the colloid-producing zone.

The particles appearing in the cathode zone immediately left the point where they appeared, moving toward the anode, and just before they reached the latter's surface, they vanished from the field of sight. No movement of particles from the anode to the cathode was observed.

When the bath voltage reached 0.9 - 1.1 volts, the ultra-microscopic picture changed fundamentally. An extremely large number of particles, as high as six to seven hundred thousand per sq mm, is formed about the cathode, in the surrounding electrolyte zone.

In the electrolysis of the most dilute solutions N/10,000 - N/2500 the colloid particles in the form of a layer begin to move away from the cathode surface immediately after their formation, first from the section closest to the anode, but later from all the cathode surface. After moving away to a distance of approximately 0.08 - 0.02 mm, the layer of colloidal particles uniformly surrounds the cathode in a solid ring about 0.15 - 0.20 mm thick, which remains fairly constant during the further course of electrolysis. In the space between the cathode surface and the inner edge of the ring we did not observe the formation of any colloidal particles, and this space was an optically inactive medium, but in the layer itself new particles are formed rather intensively, although the increase in their number could not be observed owing to the fact that the particles bend around the cathode and make their way along its surface to the region that is closest to the anode. At this point the layer of colloidal particles is drawn out into a stream that interruptedly moves toward the anode.

Thus, all the particles formed at the cathode gradually leave the cathode area for the anode, where they vanish from the field of sight. No deposit on the cathode noticeable with the microscope was observed.

This ultramicroscopic picture is shown in Photo 1, in which the following items under illumination are shown: part of the cathode surface that faces the anode; underneath it a part of the colloid layer surrounding the cathode and flowing into the general stream of particles moving toward the anode. The photograph of the cathode area was made during the electrolysis of a 3N/10,000 solution of $AgNO_3$ at a voltage of 1.1 volt and a current of 0.04 ma two minutes after the appearance of the particle layer.

In the electrolysis of solutions of $AgNO_3$ in concentrations ranging from 0.0005 N to 0.002 N, the outstanding feeture of the phenomenon observed under the ultramicroscope is the fact that the layer of colloidal particles does not leave the cathode surface at once but remains in its vicinity for some time. The length of time that the layer of particles remains in contact with the surface of the cathode depends on the concentration of the solution, increasing as the latter increases.

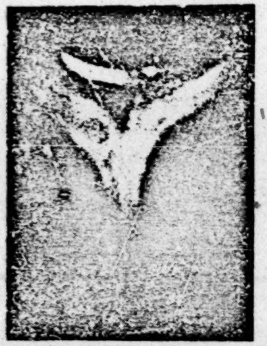

Photo 1.

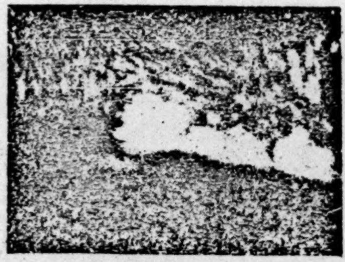

Photo 2

During the time that the layer is in direct contact with the cathode some of the colloidal particles that are closest to the cathode move toward it and are adsorbed at its surface, forming a deposit in the form of thin filaments. The higher the solution concentration, the larger the percentage of these latter colloidal particles. The rest of the particles moves toward the anode. Upon the expiration of the indicated time during which the particle layer is in direct contact with the cathode surface, the layer is observed to move away, and the nature of the phenomenon under observation becomes analogous to that taking place during the electrolysis of more dilute solutions. If the solution in the cell is agitated by moving the cathode, the picture observed under the microscope takes on its original character. The same thing happens if the circuit is broken after some time has elapsed, and then electrolysis is resumed.

In the electrolysis of solutions containing 0.003 and more gram equivalents of $AgNO_3$ per liter, the layer of colloidal particles formed does not leave the cathode surface throughout the experiment, which usually lasted at least one hour. In this case, the clearly apparent change in the quality of the colloidal systems produced must be added to the distinctive features of the observed phenomenon that depend upon the concentration of the solution. In the electrolysis of 0.003 N solutions the layer of colloidal particles formed is easy to observe, owing to the thickness it attains, some 0.15 to 0.20 mm. The colloidal particles are easy to see, apparently being of fairly large dimensions. Aggregates are often present, in the form of short thin filaments, evidently consisting of a few individual particles. The particles exhibit low mobility. As the concentration of the solution is increased, the width of the layer diminishes. The size of the colloidal particles likewise decreases, as may be judged by the increasing difficulty of observing them. Their mobility increases. In 0.05 N solutions the particle layer formed is no more than 0.075 mm thick. In it the colloidal particles are quite mobile and rather hard to follow. In the electrolysis of 0.1 N solutions we succeeded in observing the extremely thin, scintillating layer of particles only after illuminating the object quite intensively and with a magnification of no less than 400.

Quite characteristic, and varying with the solution concentration, is the observed picture of the colloidal particles participating directly in building up the metal deposit on the cathode. The participation of the colloidal particles in building the deposit is observed extremely well in the electrolysis of 0.003 - 0.005 N solutions.

This building up of a deposit on the cathode begins with the adsorption of a certain quantity of colloidal particles on the latter's surface. These particles a are joined by new ones so that within a fairly short interval of time quite thin, rather long filaments are arranged on the cathode's surface and perpendicular to the latter. New colloidal particles, which are similarly growth centers for filaments in new directions, attach themselves to the sides of these filaments -- both those already formed as well as during their formation. Thus, at the beginning the deposit looks like a herringbone, with its base at the cathode surface. Subsequently, the lateral filaments felt together as they continue to grow, forming all in all a quite flocculent layer of silver. As electrolysis continues, many new colloidal particles are formed, which constitute the material for further building up of the deposit, their filaments running in all directions.

Photo 2 shows the general nature of the phenomenon observed -- the flow of particles toward the cathode and their participation in constructing the deposit. The picture was obtained by photographing the tip of the electrode and the electrolyte zone in the vicinity of the cathode during the electrolysis of a 0.005 N solution of $AgNO_3$ with a 0.25 ma current, 3 minutes 20 seconds after the commencement of electrolysis. As the solution concentration is increased the velocity with which the particles travel to the cathode is observed to rise considerably. Owing to this latter circumstance it becomes more andmore difficult to make an accurate count of the total of the colloidal particles arising in the cathode area and to determine the percentage of particles moving toward the electrodes.

When 0.01 N solutions are electrolyzed, an approximate count is still feasible; it indicates that not less than 90% of the particles go to build up the deposit. At higher concentrations not even an approximate calculation is possible, as the time elapsing between the instant the particles appear and their deposition on the cathode is measurable in fractions of a second. For the same reason, under such electrolysis conditions adsorption on the cathode's surface can be followed visually for only a few individual particles, despite the undoubted fact of a large aggregate total of colloidal particles formed in the colloid producing zone. As the solution concentration is increased, the density of packing of the particles in the silver deposit formed on the cathode increases, the thickness of the filaments increasing and their length diminishing. Thus, they begin to look like needles, growing shorter and shorter and finally taking on the appearance of crystals scattered over the surface of the cathode when 0.1 N solutions are electrolyzed.

As may be seen from the data listed in the table, the appearance of the layer of colloidal particles in the electrolyte zone adjacent to the cathode is observed at about the same voltage but at current values (densities) that increase as the solution concentration is increased. It may be noted that the voltage does not play as much of a role as the current density. By attaching to the cell an auxiliary vessel filled with the same solution as that in the cell, we were able to move the anode farther away while leaving the cathode in the cell, thus being able to raise the voltage across the whole electrolytic cell to 2-3 times its value. Observations showed that when this was done the layer of particles appeared at about the same current values (densities).

Concentration of $AgNO_3$	Cell voltage (volts)	current (ma)	Cathode current density (amp/cm²)*	Time that particle layer remains at cathode (sec)	Particles moving to anode (%)	Brief summary of phenomena observed under microscope
0.0001	1.10	0.02	0.08	0	100	Formation of layer of colloidal particles in cathode zone of electrolyte, which immediately move away from cathode surface. All particles move to anode.
0.0002	1.10	0.03	0.12	0	100	
0.0003	1.05	0.04	0.16	0	100	
0.0005	1.05	0.06	0.24	0	100	
0.0006	1.00	0.08	0.32	5 - 8	100	Layer of colloidal particles formed remains at cathode surface for some time. During this time some of the particles participate in building up cathode deposit. Later, layer moves away from cathode, and all particles move toward anode. Percentage so doing shown at instant of departure of layer from cathode.
0.0007	1.00	0.12	0.48	10 - 15	100	
0.001	1.05	0.12	0.48	40 - 50	100	
0.002	1.00	0.14	0.56	120 - 140	100	
0.003	1.00	0.16	0.64	throughout experiment	20 -30	Particle layer formed is in contact with cathode throughout experiment. Large part of particles contribute to building cathode deposit.
0.005	1.00	0.20	0.80		20 - 25	
0.01	0.95	0.48	1.92		10	
0.025	1.00	1.2	4.80			
0.005	0.95	1.8	7.20			
0.1	0.90	3.4	13.60			

The principal features of our foregoing exposition have been listed in the table given above. The currents listed (for constant polarized cathode surface) are the minimum values and most favorable for observation of the foregoing phenomena. Increasing the current within moderate limits (2-3 times after the layer of colloidal particles has been formed in the cathode zone of the electrolyte does not affect the general character of the phenomena described above, merely making them occur more intensively.

Investigation under the ultramicroscope of the electrolysis of $AgNO_3$ solutions to which nitric acid has been added established the fact that the general nature of the phenomena observed remained unchanged on the whole. The addition of HNO_3 chiefly produces an effect analogous to that caused by increasing the concentration of silver nitrate. Thus, when N/1000 solutions of $AgNO_3$ that are also N/1000 with respect to HNO_3 are electrolyzed, the picture seen under the microscope corresponds on the whole to that observed when pure N/500 solutions of $AgNO_3$ are electrolyzed.

The effect of adding nitric acid is somewhat greater when more highly concentrated solutions are electrolyzed. For instance, when solutions are electrolyzed that are N/100 with respect to both $AgNO_3$ and HNO_3, the nature of the phenomena observed resembles the electrolysis of N/20 solutions of $AgNO_3$ more than it does that of N/50 solutions.

The electrolysis of silver-nitrate solutions containing 0.2-0.3 g of silver per 150 ml with the addition of 1 - 2 ml of nitric acid (sp. gr. 1.4) and 5 ml of alcohol, i.e., the solutions recommended by Kuster and Steinwehr [9] as the compositions most suitable for gravimetric analysis, were also subjected to ultramicroscopic investigation. When these solutions were examined under the ultramicroscope, they did not constitute optically inactive media even when placed in the cell right after they had been prepared. Moreover, even before the circuit was closed we observed the intensive formation of colloidal particles, which moved chiefly toward the sides of the cell, from which the colloidal particles spread as dense clouds throughout the solution in the cell. When the circuit was closed, all the colloidal particles moved toward the anode. A considerable number of them, formed along the cell walls behind the cathode, moved toward the anode and in passing through cathode zone of the electrolyte turned to the cathode surface with considerable velocity; they were adsorbed at the latter's surface and contributed directly to building up the cathode deposit. This phenomenon is observed no matter what current value is used in electrolysis. At currents of 1.2 - 2 ma a layer is formed in the cathode zone of the electrolyte that consists of numerous colloidal particles as a result of the course of the cathode process itself. Almost all these particles serve as material for building up the cathode deposit.

Besides acid solutions, containing nitric acid, solutions containing sulfuric, acetic, and boric acids were also subjected to electrolysis under the ultramicroscope. The results of these tests indicated that the effect of sulfuric acid upon the general character of the phenomena observed was like that of nitric acid. Acetic acid had but little effect, whereas no effect at all was observed upon the addition of boric acid

To eliminate all doubts concerning the absence of photochemical action of the light rays used for illumination (an electric arc with carbon electrodes), control tests were run in which pure solutions of $AgNO_3$ were illuminated for long periods in the cell with the circuit open. The absence of any observable formation of colloidal particles during these tests indicated the groundlessness of the doubts mentioned.

In conclusion, it may be stated that when all the conditions of electrolysis are held constant, all the phenomena described above are easily repeatable.

Evaluation of the Research results

In most of our experiments the carrying out of electrolysis at comparatively low current densities, without the evolution of gaseous products at the electrodes and with adequate isolation of the solution in the cell against the access of air made possible observation over prolonged periods of time and study of the phenomena attentively. Analysis of these phenomena enabled us to explain them and reach definite conclusions.

The identity of the ultramicroscopic pictures observed in the electrolysis of pure solutions of silver nitrate and of acid solutions of the same, even those containing alcohol (which is added, as we know, to the electrolyte, to prevent the possible formation of silver oxides), affords us sufficient justification for asserting that the colloidal systems, consisting of particles of colloidal silver, formed during electrolysis constitute a dispersed phase. The different directions taken by the individual particles moving toward the electrodes might give rise to some doubt as to the identical nature of the colloidal particles.

These doubts are likewise groundless. The modern theory of electrolyte solutions, and the doctrine of surface ion layers of colloidal particles based upon it make it possible to explain the phenomena observed under the ultramicroscope, at least qualitatively; this explanation also covers the differences in direction taken by the moving colloidal particles despite their identical nature.

The initial stage of the origin of colloidal silver particles is their formation as nuclei, which under favorable circumstances may assume the dimensions of ultramicrons.

In the electrolysis of highly diluted solutions of silver nitrate, the region of the electrolyte near the cathode is soon impoverished in silver ions, even at low current densities. The possibility that nuclei will be formed does not disappear, but the conditions for their growth are unfavorable. Under the ultramicroscope we see an optically empty space surrounding the cathode.

In principle, nuclei may be distinguished from the other colloidal particles solely by their dimensions; otherwise they possess the same properties, i.e., they bear a negative charge like the particles of colloidal silver. This charge forces them to move toward the anode, attaining the zone of the solution that is richer in positively charged ions and thus facilitates the aggregation of the nuclei to the dimensions of ultramicrons.

Under the ultramicroscope we observe a colloid-producing zone located at some distance from the cathode, in which visible colloidal particles continually appear. We observe the continuing process of the aggregation of a few colloidal particles to form larger ones. Fully formed, negatively charged, colloidal particles may be likened in principle to anions in the sense that, like the latter, they are surrounded by an ionic atmosphere, consisting mainly of positively charged ions. Owing to the adequate distance of the particles from the cathode and their low velocity, the ion atmosphere surrounding them suffers no serious deformation and hence does not deprive the particles of the possibility of moving toward the anode; this is observed under the ultramicroscope with regard to all the particles that make their appearance in colloid-producing zone. As the concentration of positively charged ions is raised, their sparseness in the area about the cathode will not make itself felt so sharply, and, naturally, the colloid-producing zone must move ever closer to the cathode's surface. Under suitable conditons the layer of colloidal particles formed therein may be in almost direct contact with the cathode surface. In this case, the ionic atmosphere around the particles that are close to the cathode will suffer serious deformation of spherical symmetry, owing to the cathode's electrostatic attraction. This inevitably gives rise to vigorous action of relaxation and electrophoretic forces, drawing the colloidal particles to the cathode and constraining them to adsorb to it.

In this deformation, i.e., in the displacement of positive and negative charges in opposite directions, the entire complex constituted by the colloidal particle and its surrounding ionic atmosphere acquires polarity. The degree of polarity must grow as the ion concentration in the solution rises, and with it the action of the forces mentioned above likewise increases, compelling the colloidal particles to move toward the cathode more energetically. The correctness of this notion of the cause of differences in the particles' directions of motion toward the electrodes is confirmed by the entirely analogous ultramicroscopic picture observed when direct current is passed through a solution of colloidal sulfur or a solution of sulfuric acid (in which a solution of colloidal sulfur is likewise formed in the cathode area and the concentration of hydrogen ions in these solutions is changed by the addition of sulfuric acid. The nature of the dispersed phase, its negative charge, and the impossibility of overcharge in the given case can arouse no doubt.

The observed ultramicroscopic picture of the direct participation of the colloidal particles in building up the deposit on the cathode is quite characteristic of the course of electrolysis of fairly dilute solutions. What has been set forth above, and the careful analysis of the research results justify the assumption that the phenomenon dealt with also exist in the electrolysis of more highly concentrated solutions. The absence of adequate visual confirmation of this is, apparently, due solely to the unfavorable observation conditions arising from the extremely short distance from the cathode of extremely small particles, which are polarized within brief intervals of time and are adsorbed at the cathode.

Nor are the current values (densities) listed in the table at which the ultramicroscope picture makes its appearance a necessary condition for the formation of colloidal particles, but merely a condition providing the optimum observation conditions, owing to the corresponding change in the ion concentration in the space about the cathode.

Evidently, the formation of colloidal particles can occur at any current densities at which the cathode process itself is feasible. The appearance of colloidal particles moving toward the anode is a signal of this. Though the ultramicroscopic picture of the participation of the colloidal particles in forming the deposit that is observed under the most favorable conditions gives the impression of the deposit being formed of colloidal particles, this is no reason to reject the possibility of even the partial construction of the deposit directly out of atoms produced as the result of the discharge of ions. Nevertheless the participation of colloidal particles is a not insignificant factor in the formation of metallic cathode deposits. As our research results indicate, , of the deposited metal and, in particular, its quantity, depend on the quality of the colloidal systems produced during electrolysis, since the departure of the colloidal particles for the anode entails a reduction in the yield per unit current.

SUMMARY

1. Investigation of the electrolysis of silver-nitrate solutions under the ultramicroscope confirmed the formation of colloidal systems as a result of the cathode process.

2. The direct participation of the colloidal particles formed during electrolysis in building up the silver deposit on the cathode was observed visually.

3. The identity of the phenomena observed in the electrolysis of pure solutions of silver nitrate and solutions to which acids had been added justifies the acknowledgment that the dispersed phase of the colloidal systems consist of silver particles.

4. Depending on the overall concentration of cations in the solution, the optimum conditions for observation of the ultramicroscopic picture are attained at definite current values.

5. The phenomena observed under the ultramicroscope are explained on the basis of the theory of electrolyte solutions.

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THE PRIORITY OF DISCOVERY OF THE SOLUTION EQUATION BY THE RUSSIAN SCIENTIST A. N. SHCHUKAREV

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In studying the problem of solution in foreign literature, and even in our own, we find that the American scientists A. Noyes and W. Whitney are supposed to have been the first to derive the solution equation for a solid substance in 1897, as described in their paper ''The rate of solution of solid substances in their own solutions'' [1].

A Noyes and W. Whitney derived the equation for the solution of a solid substance in its own solution form the very slight experimental research data on the solution of benzoic acid and lead chloride. Assuming that the solution process is based on the phenomenon of diffusion and Fick's equation, they derived this equation:

$$-\frac{dx}{dt} = c\,(s - x), \qquad (I)$$

where s is the concentration of the saturated solution, x is the concentration of the given solution at time t, c is the solution constant, and t is the time of solution.

As a result of more careful study of this question in Russian and world literature, we discovered that the scientifically established solution equation was first derived by a Russian scientist, Prof. Alexander Nikolayevich Shchukarev of the Kharkov Technological Institute at the beginning of 1896, and set forth in his paper ''Distribution of substances between two immiscible solvents" [2]. The velocity of solution of a solid body in a solvent was represented by the following equation:

$$\frac{dc}{dt} = k \cdot \pi \cdot (a - c), \qquad (II)$$

according to A.N.Shchukarev, on the basis of considerable experimental data, where k is the solution constant, c is the solution concentration at the given time t, a is the solubility limit, and π is the active surface of the solid body.

At the end of his paper, A.H. Shchukarev pointed out that the process of solution can be explained with the aid of mechanical concepts without recourse to the hypothesis of osmotic pressure or a hypothesis concerning the state of the substance.

Comparing these two solution equations (I) and (II), we see that in the Noyes and Whitney equation (I) the velocity of solution depends solely upon the solution coefficient c and the degree of saturation of the solution $(s - x)$, whereas A. N. Shchukarev makes the solution velocity depend not only on these two factors, but likewise on π, the varying surface of the dissolving body. The error of Noyes and Whitney was subsequently corrected, in 1900, by Brunner and Tollochko, who inserted the surface of the dissolving body F, missing in the equation. After this correction, the Noyes and Whitney equation looks like this:

$$-\frac{dx}{dt} = C \cdot F\,(s - x)\,, \qquad \text{(III)}$$

where F is the varying surface of the dissolving body.

It is not only the external difference between the equations proposed by A.N. Shchukarev in 1896 and Noyes and Whitney in 1897 which distinguishes these first explanations of the phenomenon of solution, but also their understanding of the essentials of the solution process itself. A.N.Shchukarev set forth the phenomenon of solution as a complex process, depending not only on the nature of the solute and the solvent, but also on the course of the process of solution. Considering the process of solution from the mechanical point of view, independent of the hypothesis of the state of the substances participating in the solution and the process of their interaction, A.N.Shchukarev developed his solution equation (II), whereas Noyes and Whitney imagined the solution phenomenon merely as a diffusion process, subject to Fick's equation. And it was on the basis of Fick's equation that they derived their solution formula (I).

The subsequent fate of these solutions (I) and (II) differed. A.N. Shchukarev's solution equation was published in the April 1896 issue of the Journal of the Russian Chemical Society, giving rise to a scientific controversy around this equation, especially involving A.A.Yakovkin and others, who spoke up at a meeting of the Russian Chemical Society on November 7, 1896, as well as in the pages of the Journal. But A.A.Baikov entered the lists in defence of A.N.Shchukarev's equation, except in cases where the soluble substances react chemically with each other.

The Noyes and Whitney equation was corrected by the researches of Brunner and Tollochko. In 1904, Nernst proved this equation and applied it to all heterogeneous processes of solution and crystallization, thus founding the theory of solution and crystallization. In the subsequent literature, the theory of solution and its equation are always cited by various authors as the work of Nernst and Noyes.

Later papers on the process of solution and crystallization pointed out the erroneousness of the Nernst-Noyes theory. Thus, as early as 1904, Shchur, investigating easily soluble salts, proposed an equation that differed from the Noyes and Whitney equation:

$$-\frac{dx}{dt} = k \lg \frac{s}{x}\,, \qquad \text{(IV)}$$

where s, x, k, and t are the same as in Equations (I) and (II).

The discrepancy between the Nernst-Noyes theory and the facts is found in papers by Ericson (1898), Auren (1901), Palmer (1906), Meyer-Wilderman (1909), Marck (1910), W.M. Fischer (1913), E.N.Gapon (1929), Drucker (1922), and others.

In his paper, "Kinetics of the separation of salts from supersaturated solutions" (1933), E. N. Gapon writes:

" The crystallization of a number of substances was found not to obey the fundamental Nernst-Noyes law. The velocity of crystallization is proportional to the second stage of supersaturation instead of to the first:

$$\frac{dc}{dt} = k \cdot \pi \cdot (a - c)^2, \qquad (VI)$$

where c, a, k, π, and t are the same quantities as in Equation (II).

The paper by Noyes and Whitney appeared more than a year after the publication of A.N. Shchukarev's paper, and even after the scientific controversy concerning the solution equation, which took place not only in Russian scientific circles, but also in Russian publications. In spite of this publicity given to A.N.Shchukarev's solution equation, neither Noyes and Whitney nor Nernst and the others, discussing this topic and all giving nearly the same equation, though a less perfect one, mentions the name of A.N. Shchukarev in their literature citations.

Priority in the discovery of the solution equation must be accorded solely to the one who was the first to derive and prove it -- the Russian scientist Prof. A.N. Shchukarev.

To shed fuller light on the development of the independent path of Russian scientific creative thought the papers of our Russian and Soviet scientists must be studied more profoundly- some papers may well be unknown to wider circles.

Not only must the priority of discoveries be defended, but so must the roads of independent advance of the scientific and inventive thought of our great Russian people, which was able to gain the greatest historical victories thanks to the correct guidance of the Bolshevist Party, led by Lenin and Stalin.

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THE PRODUCTION OF BORON FLUORIDE BY ACID METHODS

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There is no description of the technical methods for the production of boron fluoride, which is an important catalyst in many processes of organic synthesis, in the literature, although several USA factories supply compressed boron fluoride [1]. A number of articles give recipes for the laboratory preparation of boron fluoride. All the authors, with the sole exception of Hellriegel [2], who fuses KBF_4 with B_2O_3, employ the action of sulfuric acid upon a mixture of CaF_2 and B_2O_3 or on a mixture of KBF_4 (or $NaBF_4$) and B_2O_3.

The action of sulfuric acid upon a mixture of CaF_2 and B_2O_3 is the oldest method, employed by the very first researchers into the properties of boron fluoride (Davy, Berzelius). Gasselin [3] noted that the concentration of the sulfuric acid must be 66° Be to ensure steadiness in the evolution of BF_3 and the feasibility of temperatures that do not exceed 130°. Pure CaF_2 must be employed to avoid contaminating the boron fluoride by silicon fluoride, since the presence of high percentages of SiO_2 causes the mixture to swell strongly, and the BF_3 is evolved only at 125-130°. To reduce breakage of the glass flasks, Gasselin recommends that the CaF_2 be introduced only after the B_2O_3 has been dissolved in sulfuric acid.

Basarow dissolved a mixture of 100 g of CaF_2 + 100 g of B_2O_3 + 200 g of concentrated sulfuric acid at temperatures ranging from 150° to 225°.

Bowlus and Nieuwland [5] heated a mixture of 400 g of CAF_2 + 200 g of B_2O_3 + 1300 ml of concentrated sulfuric acid and purified the gas by passing it through a column containing NaF and fused B_2O_3. Zavgorodny [6] and Borneman [7] employed the same proportions.

A common feature of the methods cited is the use of considerable excesses of B_2O_3 and H_2SO_4.

	Reagent used in moles per mole of CaF_2	
	B_2O_3	H_2SO_4
Basarow	1.12	1.59
Nieuwland...........	0.56	4.75
Theoretical.........	0.33	1.0

The action of sulfuric acid upon a mixture of KBF_4 and B_2O_3 was likewise proposed by Schiff [8], who gave the following equation for the reaction:

$$6KBF_4 + B_2O_3 + 6H_2SO_4 = 8BF_3 + 6KHSO_4 + 3H_2O.$$

We list below the procedures of some other authors summarized by us.

Author	Reagent used in moles per mole of KBF_4		Remarks
	B_2O_3	H_2SO_4	
Krause, Nietsche [9]............	0.31	7.7	Mixture foams violently when smaller amounts of H_2SO_4 are used
Meerwein [10]	0.31	6.2	
Baumgarten, Hennig [11]	0.36	7.0	Heated to 270°
Baumgarten, Bruns [12]	0.2	9.6	
Booth [13]	0.26	2.02	$NaBF_4$ or NH_4BF_4 used
According to Schiff's equation	0.17	1.0	

According to Meerwein [10], the yield of BF_3 from 450 g of KBF_4 is 275-295 g, which corresponds to a yield of 0.85-0.91 of theoretical in terms of fluorine and a yield of 0.69-0.75 of the theoretical in terms of boron.

What is characteristic of all the prescriptions is the use of large excesses of B_2O_3 (as high as 100% excess) and H_2SO_4 (as high as tenfold). The lowest excess of sulfuric acid is employed by Botham, which is possibly due to the substitution of the easily soluble $NaBF_4$ or NH_4BF_4 for the poorly soluble KBF_4. This hardly compensates for the great difficulty involved in producing these salts. Unfortunately, the BF_3 yield is not indicated in the abstract accessible to us.

The experiments described below had as their object the determination of the BF_3 yield by acid methods of production as a function of the conditions employed. In particular, it was necessary to establish the size of rationally used excesses of reagents, and the effect of temperature and sulfuric acid concentration. All the authors cited above merely state that they employed concentrated acid. Lowering the acid concentration not only reduces the intensity of the reaction but ought to facilitate an increase in thesolubility of BF_3 in it (this was confirmed experimentally) and raise the moisture content of the gas.

EXPERIMENTAL

Materials

KBF_4. The hydrofluoboric acid produced by adding the stoichiometrically necessary quantity of H_3BO_3 to 20% hydrofluoric acid freed from H_2SiF_6 is precipitated with a slight excess of a saturated solution of potassium chloride. The precipitate, washed and dried at 120°, contained no Cl' or SO$_4$'' and was not titrated by an alkali in the cold i.e., contained no K_2SiF_6 . The $\frac{\text{acid F}}{\text{B}}$ ratio, determined by the Riess method [14], was 2.96.

The fluorite concentrate contained 1.03% of SiO_2 and 3.62% of B_2O_3.

The boric anhydride was prepared by dehydrating boric acid at 600° in a platinum dish. The carefully pulverized product contained 97.7% of B_2O_3.

Experimental method. The diagram of the apparatus for the generation of BF_3 by the acid method is given in Fig. 1.

Sulfuric acid and then a calculated quantity of a mixture of KBF_4 and B_2O_3 (vide infra for experiments on the decomposition of a CaF_2, B_2O_3 mixture) were placed in the 100-ml flask A. The flask was closed with a rubber stopper with capillary B, and after its contents had been well mixed together by shaking, it was immersed in a previously heated oil bath. The vigorous evolution of BF_3 began at once. The mass foamed up, its volume approximately doubling as a result of the foaming. The gas evolved was absorbed in water in the abutting Tishchenko flasks C and D. The BF_3 was wholly absorbed in the first flask, however. One hour after the start of the run, the Tishchenko flask was replaced by another, clamp F opened, and air dried by sulfuric acid in flask C was drawn through the flask by means of the aspirator E. In this procedure, it was sometimes observed that BF_3 got through to the second absorbing flask; this was manifested by the formation of a heavy fog in the right-hand portion of the first absorbing flask. Much of the fog settled within the first flask, and the escape of BF_3 to the second absorbing flask was negligible. For example, the first absorbing flask was found to contain 78.9% of the F introduced, whereas the second flask contained only 0.02%.

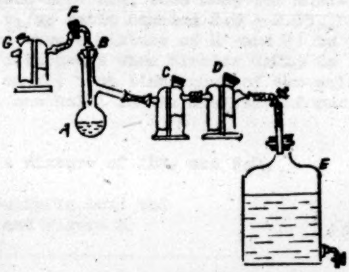


Fig. 1. Diagram of apparatus for generating BF_3 by the acid method.

Method of Analysis

The amount of BF_3 evolved was determined by analyzing the contents of the absorption vessels. In view of the fact that when BF_3 is dissolved in water, it is largely transformed into BF_4', the method employed for analysis of the solution was one based on the method of decomposing BF_4' by boiling it with a solution of $CaCl_2$ as developed by I.G. Riess [14]. The contents of the absorption flasks were transferred to a 1000-ml measuring flask, and water was added to the mark; 10 ml of the solution produced was neutralixed with a N/10 alkali against methyl orange after 10 ml of a solution of bimolar $CaCl_2$ that tested neutral against methyl orange (to bind the fluorine ion) had been added. After another 15 ml of bimolar $CaCl_2$ had been added, the solution was boiled for an hour in a flask fitted with a reflux condenser, and then quickly cooled, the condenser being washed out with a small amount of water - 15-20 ml. The solution was then finally neutralized against methyl orange with an alkali. The aggregate consumption of alkali (v_1 normal) equalled the number of milligram atoms of fluorine in the titration sample. Phenolphthalein and mannitol were added to the neutral solution, after which the boric acid was titrated with alkali. The number of milligram-atoms of boron equalled v_2 normal.

Evidently, the atomic ratio $F/B = v_1/v_2$ must equal three when pure boron fluoride is evolved. When a mixture of BF_3 and HF (or SiF_4) is absorbed, $v_1/v_2 > 3$, and when a mixture of BF_3 and $(BOF)_3$ is absorbed, $v_1/v_2 < 3$.

The percentage of SO_4'' in the absorption vessels was likewise checked in a series of tests. The ratio of the number of gram-equivalents, SO_4''/F, in the gas evolved during the first hour fluctuated within the range of 0.005-0.007, i.e., the correction required is extremely slight. During the ensuing hour the SO_4''/F ratio rose to 0.02 (see Table 1 for numerical data), due to the smaller quantity of BF_3 generated.

When HF is present in excess, its reaction with the glass may reduce the acidity slightly (by extracting alkali from the glass during the absorption period). This error will be of negligible proportions in the absorption of BF_3 or, more particularly, of a mixture of BF_3 and $(BOF)_3$.

During this stage of the work, it was discovered that when KBF_3 was analyzed by decomposition with 1-molar $CaCl_2$, the v_1/v_2 ratio equaled 2.9 - 2.95, apparently because of the reaction taking place when a mixture of $H^{\cdot}$ and F' is boiled together with glass [14]. This effect disappears when bimolar $CaCl_2$ is used, apparently because of the concentration of F'; but since much of the acidity was neutralized in the cold (usually about one half) in the analysis of our solutions, this error was of minor importance.

Preparation of BF_3 by the Decomposition of a Mixture of KBF_4 and B_2O_3

1. Influence of Concentration of Sulfuric Acid and Temperature (Table 1 and Figure 2)

Table 1

Influence of Concentration of Sulfuric Acid Upon Decomposition of KBF_4 50% Excess B_2O_3 — 20% Excess H_2SO_4 *

Test No.	Temperature	H_2SO_4 concentration %	BF_3 yield ** and F/B ratio during:							Overall yield of BF_3 (%)
			First Hour			Second Hour		Third hour		
			Yield (in %)	F/B	gram equivalent ratio SO_4/F	Yield (in %)	F/B	Yield (in %)	F/B	
1	180°	95.5	37.6	3.18	0.006	6.1	3.56	4.0	3.72	47.7
2	180	99.5	52.8	3.36	—	5.9	3.42	5.3	2.97	64.0
3	180	99.5	52.3	2.97	0.007	6.5	3.38	4.8	3.33	63.6
4	180	105.9	67.6	3.05	0.005	8.0	3.22	3.5	3.19	79.1
5	150	95.5	2.8	3.62	—	1.4	3.39	5.3	3.17	9.5
6	150	99.5	29.0	2.97	—	4.0	2.98	9.6	3.18	42.6

---

* The amount of reagent was computed from the following equation :

$$6\ KBF_4 + B_2O_3 + 6H_2SO_4 = 8BF_3 + 6KHSO_4 + 3H_2O$$

** Here, as in the following experiments, the amount of BF_3 generated was computed in terms of the substance that was present in lesser proportion in the absorption vessel — boron when $F/B > 3$, and fluorine when $F/B < 3$. The yield of BF_3 is in terms of the stoichiometrically possible.

The increase in the concentration of sulfuric acid makes the F/B ratio approach 3, apparently owing to the decrease in the hydrolysis of the BF_3. When 95.5% H_2SO_4 is used, an abundant condensation of the hydrate of BF_3 is observed in the upper section of the reaction flask and in the outlet tube. When 99.5% H_2SO_4 is used, the quantities of the hydrate of BF_3 formed are extremely small, and when oleum (105.9 % H_2SO_4) is used, completely dry gas is generated. At the same time the amount of sulfur trioxide entrained by the boron fluoride does not increase: evidently, the rapid formation of $KHSO_4$ and $K_2S_2O_7$ sharply reduces the vapor tension of the SO_3 above the mixture.

When oleum was used in the absorption vessels, the amount of SiO_2 evolved was negligible. When 95.5% H_2SO_4 was used, the quantity of SiO_2 (i.e., the SiF_4 evolved as well) was considerably higher. The extremely high value of the F/B ratio likewise testifies to this fact. The relative contamination of the gas by silicon fluoride increased sharply after the first hour.

We found the highest percentage of BF_3 generated in working with oleum. This indicates that in the industrial application of the process, oleum should be employed; there is all the more reason for so doing in that the use of the monohydrate is very much less convenient owing to the high temperature at which it solidifies.

Comparison of the results of tests 1-2 and 5-6 (Table 1) clearly indicates the favorable effect of raising the temperature of the reaction mixture during the course of decomposition. On the basis of the data cited, we employed oleum at a temperature of 180° in running our subsequent decomposition experiments.

2. Effect of an Excess of Oleum

In Table 2 and Fig. 3 we have given the results of tests of the decomposition of mixtures of KBF_4 with a 50% excess of B_2O_3 at 180° under the action of oleum (105.9% H_2SO_4).

Table 2

Effect of an Excess of Oleum

Test No.	Excess H_2SO_4 (in % of stoichiometrical quantity	BF_3 and F/B ratio during:							Overall yield of BF_3 (%)
		First Hour			Second Hour		Third Hour		
		Yield (in %)	F/B	gram equivalent ratio SO_4F	Yield (in %)	F/B	Yield in %	F/B	
7	100	50.9	3.06	0.005	8.4	3.16	2.3	2.95	61.4
4	200	67.6	3.05	0.005	8.0	3.22	3.5	3.19	79.1
8	300	73.7	3.02	0.005	2.1	4.17	4.4	3.6	80.2

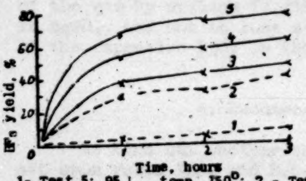
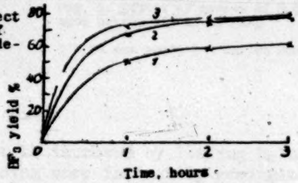


Fig. 2. Effect of the concentration of acid and temperature upon the decomposition of KBF_4.

1- Test 5: 95.5% temp. 150°; 2 - Test 6: 99.5%, temp. 150°; 3 - Test 1: 95.5% temp. 180°; 4 - Test 2: 99.5% temp. 180°; 5 - Test 4: oleum, temp. 180°.

Fig. 3. Effect of excess of oleum upon decomposition of KBF_4.



1 - Test 7: 100%; 2 - Test 4: 200%; 3 - Test 8: 300%.

The yield of boron fluoride rises considerably when the excess of oleum is raised from 100% to 200%. Any further increase in this figure raises the BF_3 yield but little and must be acknowledged to be inadvisable. The contamination of the BF_3 by sulfur trioxide does not depend upon the amount of oleum used (Table 2, Tests 7 and 8).

3. Effects of an Excess of B_2O_3

The results of a series of tests run at 180° with an excess of 200% of oleum (105.9% H_2SO_4) for various quantities of B_2O_3 are shown in Table 3 and Fig. 4.

Thus, the employment of considerable excesses of the expensive B_2O_3 as reccommended in the literature not only does not improve the yield of BF_3, but actually lowers it; this is apparently due to the formation of $B_2O_3 \cdot BF_3$ in the liquid phase. The sole advantage of using an excess of B_2O_3 is a reduction of the F/B ratio, which does not rise much above 3, however, during the period when most of the BF_3 is generated (the first hour), if the stoichiometrical quantity of B_2O_3 is employed.

Table 3

Effect of an Excess of B_2O_3

Test No.	B_2O_3 Excess %	BF_3 and F/B ratio during:						Overall yield of BF_3 (in %)
		First Hour			Second Hour			
		Yield %	F/B	Gram equivalent ratio SO_4/F	Yield %	F/B	Gram equivalent ratio SO_4/F	
9	0.0	76.7	3.14	0.003	5.3	3.95	0.02	82.0
10	0.0	76.0	3.10	-	5.3	4.17	—	81.3
13	0.0	—	—	—	81.8	3.15	—	81.8
11	10.0	72.9	3.24	—	7.2	3.55	—	80.1
12	20.0	74.8	3.03	0.004	6.8	3.53	0.016	81.4
4	50.0	67.6	3.05	0.005	8.0	3.22	—	75.6
14	200.00	—	—	—	58.1	2.90	—	58.1

It is probable that this ratio is increased due to the free HF, whereas SiF_4, or carrying out of the reaction in metallic vessels, causes this ratio to approach 3, owing to the elimination of the otherwise possible reaction with the glass walls of the vessel and the resulting low percentage of SiO_2 in the KBF_4. In any case, it is better, if necessary, to improve the composition of the gas by washing it with a solution of B_2O_3 in H_2SO_4, and not to lose a considerable amount of the expensive B_2O_3 in the decomposition sludge.

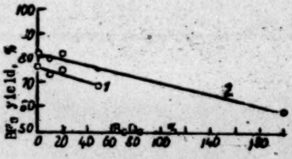


Fig. 4. Effect of excess of B_2O_3 upon decomposition of KBF_4.

1 - In one hour; 2 - in two hours.

4. Decomposition of Fused KBF_4 and H_3BO_3

To find out whether the yield of BF_3 would not be improved by letting H_2SO_4 act upon fused KBF_4 and B_2O_3 (the components thus being more intimately comingled), we ran corresponding preliminary experiments. These tests confirmed the observavation made by Hellriegel [2] that BF_3 is generated intensively when H_2BO_3 or B_2O_3 is introduced into fused KBF_4. Thus, for example, when 50 g of KBF_4 and 7 g of B_2O_3 are fused at a temperature of about 600°, a considerable amount of BF_3 gas was evolved. The loss in weight of the KBF_4 constituted 9.2%.

When strong sulfuric acid (99.5% H_2SO_4), used in 300% excess, was allowed to act upon the fused mixture and the heating time was 2 hours, the BF_3 yield amounted to 78.8% with the F/B ratio in the gaseous phase equaling 2.78.

Thus, fusing KBF_4 with B_2O_3 does not increase the yield of BF_3 and, hence, is inadvisable; this is all the more so because part of the BF_3 is lost during fusion.

5. Decomposition of a Fluorite Concentrate

The decomposition of a fluorite concentrate by sulfuric acid in the presence of B_2O_3 was effected in conditions resembling those used for KBF_4 and in the very same apparatus (Fig. 1).

Sulfuric acid was placed in the flask, and a calculated quantity of a finely powdered mixture of fluorite concentrate and B_2O_3 was poured in. After the contents were carefully stirred, the flask was immersed in an oil bath that had been previously heated. When oleum was used, the reaction mass was observed to heat up markedly and foam up after the mixture of CaF_2 and B_2O_3 had been added; sometimes pulp was thrown up. To eliminate the violent foaming of the reaction mass the reagents were mixed together under somewhat different conditions, namely: about 1/3 of the oleum was first poured into the flask, after which the mixture of CaF_2 and B_2O_3 was poured in, the mass carefully stirred (by shaking) and then placed in the oil bath. The remaining acid (oleum) was added gradually, during the space of 10-15 minutes, from a dropping funnel, which was mounted by means of rubber stopper in the upper portion of the flask. When this method of adding the acid was used, we were able to eliminate the ejection and violent foaming of the reaction mass. The generated BF_3 was absorbed in water in Tishchenko bottles, as before. The quantity of BF_3 absorbed was determined by the method described above.

In table 4 there are listed the results of tests* of the decomposition of

Table 4

Decomposition of a Mixture of CaF_2 and B_2O_3 by Sulfuric Acid

Test No	Temperature in °C	Concentration of H_2SO_4 %	Excess of H_2SO_4 (in % of stoichiometrical quantity)	BF_3 yield and F/B ratio during				Overall yield of BF_3 %
				First Hour		Second Hour		
				Yield %	F/B	Yield %	F/B	
1	150	92.0	100	0.55	2.80	8.10	2.75	8.6
2	150	105.9	100	15.83	2.94	6.55	2.78	22.4
3	180	92.0	200	22.73	2.47	13.15	2.63	35.9
4	180	105.9	100	39.91	2.91	24.51	2.73	64.4
5	180	105.9	200	52.36	2.84	14.29	2.69	66.6

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* The quantities of reagents were calculated from the reaction:

$$3CaF_2 + 3H_2SO_4 + B_2O_3 = 2BF_3 + 3\,CaSO_4 + 3H_2O.$$

a mixture of fluorite concentrate and B_2O_3 by sulfuric acid, the B_2O_3 being used in 50% excess over its stoichiometrical quantity.

The data indicate that, as in our experiments with KBF_4, increasing the concentration of sulfuric acid makes the F/B ratio approximate 3 and increases the yield of BF_3 considerably. The yield of boron fluoride is increased by increasing the excess of sulfuric acid and raising the temperature of the reaction.

The very low value of the F/B ratio in the absorption vessels is worthy of note. We did not elucidate the reasons for this, as the method of preparing BF_3 from fluorite was clearly inferior to the method using KBF_4.

CONCLUSIONS

On the basis of our research, it may be assumed that when mixtures of KBF_4 and B_2O_3 are decomposed by oleum "Method 1" with the use of a stoichiometrical amount of B_2O_3 and of a 200% excess of oleum, the yield of BF_3 may rise as high as 80% at 180°. When mixtures of CaF_2 and B_2O_3 are decomposed by oleum using a 50% excess of B_2O_3 and a 100% excess of oleum, the yield of BF_3 is 65% at the same temperature.

When Method 1 is employed, a number of simple operations (precipitation, filtration, and drying) must be performed for the production of KBF_4, which almost entirely eleiminates the extremely unpleasant operation of dehydrating the B_2O_3, which also inevitably involves losses of the expensive boric acid that have not been considered in the foregoing discussion. The cost of the materials employed in Method 1 may be further reduced by realizing the method of producing "fluoboric acid" by the interaction of fluorite, boric acid, and dilute sulfuric acid, investigated by V.S.Yatlov and G.D. Malbin.

It should also be borne in mind that the decomposition of KBF_4 + B_2O_3 mixtures takes place more smoothly, and with less foaming, than the decomposition of CaF_2 + B_2O_3 mixtures, and that removing the fused "bisulfite" from the reaction apparatus is much simpler than removing the "plaster" formed in Method 2.

It may therefore be assumed that Method 1 is to be preferred, not only in the laboratory preparation of BF_3, but also in the industrial application of the acid method for its production.

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VISCOSITY AND DENSITY OF BINARY MIXTURES OF NICOTINE. I

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The present research was inaugurated with the aim of learning the nature of the interaction of nicotine with phenol, acetic acid, and water.

Nicotine has been known since 1828 [1]; its physical and chemical properties have been studied but little, however.

Jepcott [2], Hudson [3], and Tsakalotos [4], noticing in their studies of viscosity, density, specific rotation, and index of refraction, that considerable heat was evolved by mixing nicotine and water, believed that hydrates are formed by nicotine and water. Dezelic [5], in his investigation of the viscosity, density, and refractive index of mixtures of nicotine and acetic acid at the one temperature of 20°, points out the formation of the compound $C_{10}H_{14}N_2 \cdot 3C_2H_4O_2$. In Étard's opinion [6], the compound $C_{10}H_{14}N_2 \cdot C_2H_4O_2$ is formed by nicotine and acetic acid. Pinner [7], however, considers the formation of such a compound to be unlikely.

EXPERIMENTAL

Our study of the binary systems: nicotine – phenol, nicotine – acetic acid, and nicotine – water was effected by the method of viscosity and density at three temperatures. The temperature in the thermostat was held constant within ± 0.1°. Viscosity was measured in a viscosimeter for volatile liquids [8]. Density was measured at a temperature of 25° by a pycnometer with a capacity of 1.815 ml.

Our nicotine base was prepared by us from a 40% aqueous solution of nicotine sulfate. The aqueous solution of nicotine sulfate was treated with a solution of caustic alkali. Then the nicotine was extracted from this solution by means of sulfuric ether. The ether was driven off from the extract, and the nicotine was slowly dried over fused caustic alkali. The nicotine was repeatedly distilled in vacuum, and the middle fraction was taken; this fraction possessed the following constants: b.p. 111.0-112.0° at 6 mm.

Temperature	25°	35°	50°	75°
Density	1.0068	0.9986	0.9866	0.9670
Viscosity	3.8942	3.1555	2.0376	1.2626.

The indicated values of viscosity and density are the mean values of a series of determinations. The values reported in the literature are:

Temperature ..	0°	10.0°	20.0°	30.0°	
Density.......	1.02556	1.01726	1.00906	1.00094	
Temperature...	40°	50.0°	60.0°	70.0°	80.0° [1]
Density.......	0.99286	0.98481	0.97679	0.96871	0.96057

d_4^{10} 1.0180; d_4^{20} 1.0097; d_4^{20} 1.0092; $d_4^{22.4}$ 1.0121 [9]; d_4^{20} 1.00924;
$\eta_{20°}$ 4.54 [10].

The prepared nicotine, which was completely colorless, was kept in a bottle with a cork stopper. As nicotine gradually turns yellow upon standing, it was subjected to vacuum distillation every day or two under the same conditions. When this was done, the nicotine's constants did not change.

The phenol was purified by double distillation and subsequent fractional crystallization. The melting point of the purified phenol was 41°.

The acetic acid was dessicated with calcined copper sulfate until new batches of the latter did not turn blue upon standing. Thereupon the acid was separated from the copper sulfate and distilled at a temperature of 116.0-117.0°. The fraction distilled over at this temperature was frozen. An acid with a m.p. of 16.60° was obtained after this freezing was performed twice. Double-distilled water was used.

NICOTINE – ACETIC ACID SYSTEM

The results of measuring the viscosity and density are listed in Table 1 and shown graphically in Figs. 1 and 2. The viscosity isotherms have sharp maxima at 25 mol.% of nicotine. The density isotherms likewise pass through a maximum value. When the components are mixed together intense heating is observed.

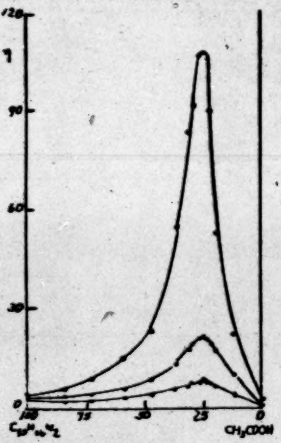

Fig. 1.

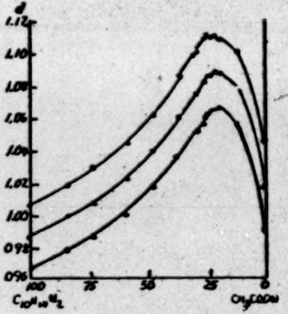

Fig. 2.

Table 1
Nicotine -- Acetic Acid

Nicotine mol.%	Viscosity			Density		
	25°	50°	75°	25°	50°	75°
0.00	1.2414	0.8724	0.5974	1.0459	1.0170	0.9888
11.69	23.0437	7.7773	3.7762	1.1010	1.0789	1.0569
19.85	74.9779	18.1158	7.0018	1.1101	1.0885	1.0673
21.29	93.4620	20.8027	7.4297	1.1104	1.0889	1.0662
23.69	109.9025	21.6277	7.5042	1.1108	1.0863	1.0641
24.89	111.9087	22.0874	7.6179	1.1118	1.0857	1.0630
26.02	110.8937	21.7225	7.4415	1.1100	1.0832	1.0576
29.52	94.1461	19.4717	6.7915	1.1008	1.0749	1.0524
30.62	86.5565	18.6494	6.5005	1.0997	1.0742	1.0500
37.11	56.3141	13.2105	5.1660	1.0860	1 0607	1.0370
47.00	24.1021	7.7086	3.4461	1.0622	1.0398	1.0181
58.88	15.2012	5.2078	2.5134	1.0449	1.0221	1.0001
73.06	8.7511	3.6097	1.9164	1.0294	1.0073	0.9868
84.35	7.0722	3.0848	1.7226	1.0223	1.0001	0.9797
100.00	3.8942	2.7376	1.2626	1.0068	0.9866	0.9670

NICOTINE - PHENOL SYSTEM

The results of measuring the viscosity and density are listed in Table 2 and shown graphically in Figs 3 and 4.

Table 2
Nicotine -- Phenol

Nicotine mol %	Viscosity			Density		
	35°	50°	75°	35°	50°	75°
0.00	6.0320	3.5352	1.7808	1.0646	1.0508	1.0294
10.04	16.2795	7.2241	2.9122	1.0684	1.0543	1.0328
20.60	28.7207	11.4623	4.0962	1.0657	1.0616	1.0296
22.05	29.7267	11.8977	4.1494	1.0636	1.0497	1.0295
24.09	30.0697	12.1491	4.3757	1.0616	1.0493	1.0267
25.30	29.8266	12.0600	4.2857	1.0611	1.0490	1.0265
25.50	29.6908	12.0500	4.2588	1.0608	1.0486	1.0260
26.29	29.4018	12.0031	4.2022	1.0606	1.0474	1.0256
28.65	28.6366	11.7369	4.1821	1.0589	1.0464	1.0234
30.78	27.5496	11.6292	4.1714	1.0578	1.0438	1.0232
40.35	21.0062	10.0798	3.7116	1.0481	1.0344	1.0137
49.81	16.1628	8.0922	3.3540	1.0380	1.0268	1.0051
66.36	7.4225	4.7965	2.4255	1.0231	1.0103	0.9905
79.61	5.1621	3.4095	1.8664	1.0131	1.0008	0.9805
86.10	4.5023	3.0825	1.7553	1.0092	0.9962	0.9768
100.	3.1555	2.0376	1.2626	0.9986	0.9866	0.9670

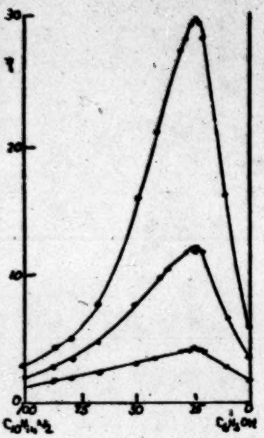

Fig. 3

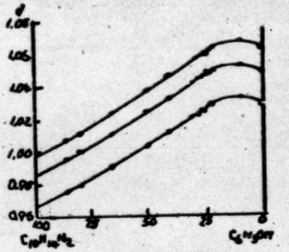

Fig. 4

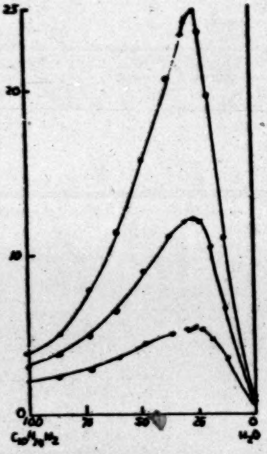

Fig. 5

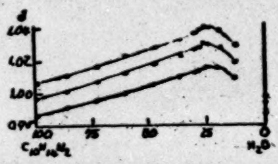

Fig. 6

The isotherms of viscosity pass through maxima that are shifted somewhat toward the more viscous component, at 23-34 mol.% of nicotine. The density isotherms likewise pass through maxima. When the components are mixed together, the liberation of considerable heat is observed.

NICOTINE – WATER SYSTEM

The results of measuring the viscosity and density are listed in Table 3 and shown graphically in Figs. 5 and 6.

Table 3
Nicotine -- Water

Nicotine mol.%	Viscosity			Density		
	25°	35°	50°	25°	35°	50°
0.00	0.8941	0.7205	0.5497	0.9971	0.9941	0.9881
12.02	11.1221	6.6290	3.4358	1.0307	1.0192	1.0089
19.77	19.9609	10.4012	4.7713	1.0391	1.0293	1.0169
24.24	23.8328	12.0832	5.3816	1.0406	1.0316	1.0159
25.92	25.1908	12.2377	5.4934	1.0413	1.0300	1.0158
28.08	24.4267	12.1881	5.4027	1.0398	1.0293	1.0140
30.47	23.6034	12.1004	5.3037	1.0369	1.0265	1.0135
36.92	21.0282	11.1518	5.1461	1.0340	1.0241	1.0105
48.52	15.8446	8.8172	4.4260	1.0288	1.0185	1.0067
60.52	11.4298	6.5720	3.6237	1.0246	1.0128	1.0015
72.85	7.9538	4.8325	2.8344	1.0174	1.0073	0.9968
86.35	5.0141	3.8106	2.4862	1.0144	1.0055	0.9924
100.00	3.8942	3.1555	2.0376	1.0068	0.9986	0.9866

The viscosity isotherms pass through maxima that shift from 25 mol% to 27 mol. % of nicotine with increase in temperature. The density isotherms likewise pass through maxima. Heating is observed when the nicotine–water mixture is prepared.

Evaluation of Results

Let us consider the nicotine – acetic acid system. The viscosity isotherms obtained by us for this system all pass through maxima corresponding to 25 mol.% of nicotine. The location of the maxima does not change as the temperature is varied, the rational proportion of components remaining the same. These systems are of the rational type [11,12], and, hence, the location of the maxima on the viscosity isotherms gives the composition of the compounds existing in the liquid phase. Thus, we established from the viscosity diagram of this system that the compound has the composition $C_{10}H_{14}N_2 \cdot 3CH_3COOH$. As we have already stated, Etard [8] established the existence of an equimolecular compound of nicotine and acetic acid. It is possible that a compound exists in which there are two molecules of acid for each molecule of nicotine, but in the viscosity isotherms there is reflected only a compound consisting of one molecule of nicotine and three molecules of acid as possessing the highest viscosity. In this case we may be dealing with a situation that is similar to what was pointed out by Udovenko [13] for irrational systems

The problem of which of these three compounds may exist in the solid state can be solved unequivocally only by means of a thermal analysis.

The nicotine – phenol system is in the main similar to the nicotine – acetic acid system, but the viscosity maximum is displaced somewhat toward the more viscous component, being located at 76-77 mol.% of phenol. This position of the maximum on the viscosity isotherms indicates the presence of a compound with the composition $C_{10}H_{14}N_2 \cdot 3C_6H_5OH$, which dissociates slightly into its components.

The viscosity maximum on the 25° isotherm in the nicotine – water system lies at about 75 mol.% of water. But, as the temperature is raised, it shifts slightly toward the nicotine side, as the more viscous component, lying at 73 mol.% of water on the 50° isotherm. The location of the maxima on the viscosity isotherms indicates the formation of a compound of the composition $C_{10}H_{14}N_2 \cdot 3H_2O$, which dissociates slightly into its components as the temperature is raised, as a result of which the maximum shifts toward the more viscous component. In this respect the nicotine – water system must be classed as an irrational one.

The density isotherms of the nicotine – acetic acid system (Fig. 2), the nicotine – phenol system (Fig. 4), and nicotine – water system (Fig. 6), which have a singular shape, are doubless of some interest. The maxima in the viscosity and density diagrams of the nicotine – water and nicotine – acetic acid systems correspond to identical molecular proportions. In the nicotine – phenol system, however, the viscosity maximum lies at the same composition as in the previous ones, whereas the density maximum is displaced toward the nicotine end.

In conclusion, I wish to express my sincere gratitude to Prof. V.V. Udovenko for his valuable counsel and advice, which aided me in performing this research.

CONCLUSIONS

1. The viscosity and density of the nicotine–acetic acid system was investigated at the following temperatures: 25, 50, and 75°.

2. The viscosity and density of the nicotine – phenol system was investigated at the following temperatures: 35, 50, and 75°.

3. The viscosity and density of the nicotine – water system was investigated at the following temperatures: 25, 35, and 50°.

4. It was found that compounds of the following composition:

$C_{10}H_{14}N_2 \cdot 3CH_3COOH$, $C_{10}H_{14}N_2 \cdot 3C_6H_5OH$ and $C_{10}H_{14}N_2 \cdot 3H_2O$

are formed in the nicotine – acetic acid, nicotine – phenol, and nicotine – water systems, respectively.

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VISCOSITY AND DENSITY OF BINARY MIXTURES OF NICOTINE. II*

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In our preceding paper [1] we established the presence of a compound of nicotine and acetic acid corresponding to the formula:

$$C_{10}H_{14}N_2 \cdot 3CH_3COOH.$$

The present research was inaugurated to elucidate the nature of the interaction of nicotine with acids that are weaker than acetic acid, namely, butyric, oleic, and stearic acids.

NICOTINE – (NORMAL)–BUTYRIC ACID

Commercial butyric acid was employed, it being subjected to triple distillation with a dephlegmator after a preliminary desiccation over anhydrous copper sulfate; its b.p. was 159.5° at 700 mm. The nicotine had the same constants as in the preceding paper [1].

The results of measuring the viscosity and density are given in Table 1 and shown graphically in Figs. 1 and 2.

Table 1 Nicotine - Butyric Acid

Nicotine mol. %	Viscosity			Density		
	25°	50°	75°	25°	50°	75°
0.00	1.4691	0.9885	0.7283	0.9538	0.9274	0.9021
9.90	11.7410	5.1881	2.8001	1.0008	0.9773	0.9526
19.92	48.6918	14.2394	5.7201	1.0270	1.0034	0.9799
21.39	52.3870	14.8951	5.8716	1.0285	1.0052	0.9815
22.77	53.8238	15.0436	5,9487	1.0290	1.0067	0.9820
23.40	53.9675	15.1308	5.9923	1.0305	1.0069	0.9823
24.78	54.2007	14.9924	5.9179	1.0308	1.0075	0.9829
27.07	53.8677	14.8904	5.8579	1.0298	1.0063	0.9830
29.93	50.7657	13.9020	5.6875	1.0296	1.0063	0.9848
38.72	29.6106	9.4601	4.0824	1.0255	1.0022	0.9834
50.11	17.5547	[illegible]	3.0825	1.0213	0.9987	0.9778
60.81	11.6317	4.4621	2.3594	1.0183	0.9965	0.9762
69.70	8.4040	3.7664	2.0727	1.0160	0.9949	0.9742
80.40	6.2651	2.9829	1.7335	1.0140	0.9917	0.9718
89.28	5.1919	2.5789	1.5396	1.0111	0.9893	0.9700
100.00	3.8942	2.0376	1.2626	1.0068	0.9866	0.9670

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*A. A. Sheverdin, laboratory assistant, participated in carrying out the experimental section of this research.

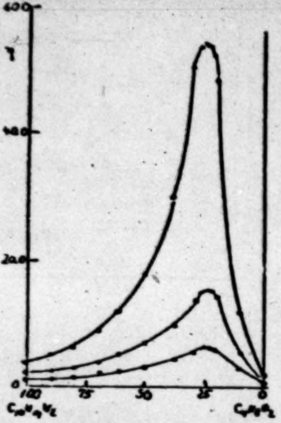

Fig. 1

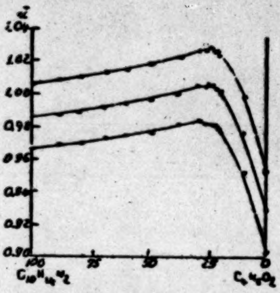

Fig. 2

The viscosity isotherms pass through maxima that correspond to 24 mol.% of nicotine; the maxima exhibit no appreciable shift as the temperature is raised. The density isotherms likewise pass through maxima that are located at the same molecular compositions as the maxima on the viscosity isotherms. In preparing these mixtures, the heating observed was especially pronounced when the composition approached the values corresponding to the maxima on the viscosity diagram.

NICOTINE – OLEIC ACID SYSTEM

The oleic acid was prepared from a chemically pure preparation by double distillation in vacuum. The fraction distilled over at 224° and 9 mm, with a m.p. of 14°, was used.

The results of measuring the viscosity and density are listed in Table 2 and are shown graphically in Figs. 3 and 4. The viscosity isotherms pass through maxima that are located at 23.5 mol.% of nicotine. There is a slight inflection in the density isotherms, that is situated at about the position of the maxima on the viscosity isotherms. During the preparation of the mixtures, heating was observed, which was most noticeable at the solution concentrations corresponding to the situation of the maxima in the viscosity diagrams.

NICOTINE – STEARIC ACID SYSTEM

Chemically pure stearic acid, with a m.p. of 69.4°, was used in the experiments. The results of measuring the viscosity and density are listed in Table 3. In Fig. 5 there is shown the viscosity diagram for this system. The density diagram exhibits no points of special interest and is therefore not shown here. The system was fully investigated only at 75°. A mixture containing more than 60 mol.% of stearic acid crystallized at the temperatures of 25 and 50°. The viscosity isotherms have maxima at 22.5 mol.% of nicotine. Slight heating was observed during

Table 2
Nicotine — Oleic Acid

Nicotine Mol.%	Viscosity			Density		
	25°	50°	75°	25°	50°	75°
0.00	35.4084	14.3838	7.2624	0.8950	0.8755	0.8578
10.49	74.2677	22.1297	9.4913	0.9081	0.8824	0.8718
19.89	106.9814	29.2818	11.0375	0.9226	0.9091	0.8824
20.16	107.9520	29.5604	11.0460	0.9231	0.9034	0.8851
21.32	110.3440	30.0278	11.2521	0.9243	0.9051	0.8869
21.75	110.4118	30.1514	11.3085	0.9246	0.9069	0.8878
23.46	112.3137	30.4850	11.8245	0.9246	0.9070	0.8880
24.82	110.3192	30.1271	11.7371	0.9262	0.9070	0.8895
24.89	109.9523	30.1152	11.6797	0.9265	0.9071	0.8897
26.01	109.3111	30.0957	11.5159	0.9266	0.9077	0.8909
28.26	105.3402	28.7680	10.8849	0.9278	0.9111	0.8926
29.80	102.5190	28.0183	10.5561	0.9300	0.9133	0.8956
41.02	73.4781	22.1918	9.1618	0.9378	0.9214	0.9031
48.41	51.8377	17.6026	7.5826	0.9440	0.9253	0.9086
59.48	34.1939	12.3453	5.7842	0.9552	0.9370	0.9198
70.31	20.1229	8.1356	4.1360	0.9662	0.9471	0.9295
79.39	11.7011	5.1975	2.8660	0.9777	0.9576	0.9408
89.75	7.2764	3.4316	2.0399	0.9913	0.9727	0.9530
100.00	3.8942	2.0376	1.2626	1.0068	0.9866	0.9670

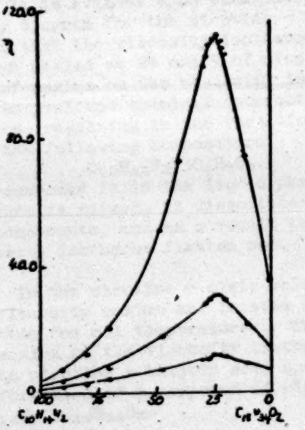

Fig. 3

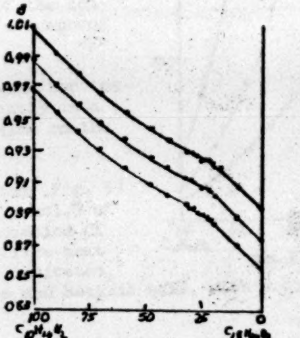

Fig. 4

Table 3
Nicotine – Stearic Acid

Nicotine Mol.%	Viscosity			* Density		
	25°	50°	75°	25°	50°	75°
0.00	—	—	8.1362	—	—	0.8447
11.49	—	—	10.6377	—	—	0.8595
18.18	—	—	12.3841	—	—	0.8635
20.24	—	—	12.8388	—	—	0.8675
20.69	—	—	12.8544	—	—	0.8678
22.83	—	—	13.0609	—	—	0.8698
25.06	—	—	12.8246	—	—	0.8726
26.59	—	—	12.3627	—	—	0.8739
29.71	—	—	11.7467	—	—	0.8769
39.91	—	26.0361	10.0460	—	0.9026	0.8871
49.52	—	18.6046	8.0003	—	0.9138	0.8972
60.34	—	12.3042	5.7612	—	0.9270	0.9104
69.86	21.1780	8.5707	4.5904	0.9563	0.9401	0.9230
79.61	14.2227	6.0452	3.2500	0.9721	0.9540	0.9383
89.73	7.7900	4.0025	2.1965	0.9874	0.9703	0.9512
100.00	3.8942	2.0376	1.2626	1.0055	0.9686	0.9670

preparation of the mixtures; this heating was especially marked at the same solution concentrations as in the previous systems.

Evaluation of Results

It is evident upon examination of the viscosity diagram for the nicotine – butyric acid system that the viscosity isotherms all pass through maxima at 24 mol.% of nicotine. The presence of maxima on the viscosity isotherms testifies to profound chemical interaction of the components, resulting in the formation of a compound with the following composition:

$$C_{10}H_{14}N_2 \cdot 3C_4H_8O_2.$$

This compound is in the liquid phase; when the temperature is raised, it dissociates slightly into its components, and as a result the maxima on the viscosity isotherms flatten out.

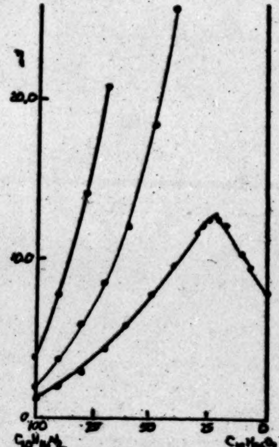

Fig. 5

In the nicotine – oleic acid system (Fig. 3) the viscosity maxima are located at 23.5 mol.% of nicotine for all temperatures. This location of the maxima on the viscosity isotherms, like that in the nicotine – butyric acid system, indicates the formation of a compound of nicotine and butyric acid, with a composition of $C_{10}H_{14}N_2 \cdot 3C_{18}H_{34}O_2$.

In the nicotine- stearic acid system we are able to investigate the viscosity and density of the mixtures only at 75°, as pure stearic acid melts at 69.4°, and therefore mixtures containing more than 60 mol.% of the latter crystallize at 25 and 50°. The viscosity isotherm passes through a maximum at 22.5 mol% of nicotine, which indicates the existence in the liquid phase of a compound with the formula: $C_{10}H_{14}N_2 \cdot 3C_{18}H_{36}O_2$. The density isotherms, which pass through maxima that correspond to the composition of the compound formed in the system of nicotine – butyric acid (Fig. 2), are likewise of interest.

In the nicotine – oleic acid system (Fig. 4), there is also a point of inflection on the density isotherms, corresponding to the composition of the compound formed.

Our experimental data demonstrate that nicotine forms compounds with butyric, oleic, and stearic acids, as it does with acetic acid, which contain three molecules of the acid per molecule of nicotine.

A large enough number of systems in which the viscosity isotherms resemble those studied by us are reported in the literature [2,3,4,5,6]. The existence of chemical compounds in these systems has also been proved by other methods of physico-chemical analysis. But, as Udovenko [7] has pointed out, it often happens that the viscosity diagrams reflect the existence of compounds of more complex composition than that which crystallizes out in solid form. This occurs whenever the simpler compound formed can react with one of the system's components, giving rise to a more complex compound, which in turn is reflected in the viscosity isotherms. Therefore, the existence of complex compounds in the solution, which have high viscosity, does not exclude the possibility of the existence of other compounds in the same system, with lower viscosity. In agreement with Udovenko, we believe that the systems investigated by us must contain compounds of nicotine with one and two acid molecules, in addition to compounds of nicotine with three acid molecules. Such compounds of nicotine with mineral acids have been reported in the literature [8].

It is quite possible that thermal analysis may make us able to prove the existence of these compounds in systems with organic acids as well.

SUMMARY

1. The viscosity and density of the nicotine – butyric acid and nicotine – oleic acid systems were investigated at the temperatures of 25, 50, and 75°, and those of the nicotine – stearic acid system at 75°.

2. It was established that the components of these systems react with each other, forming the following compounds: $C_{10}H_{14}N_2 \cdot 3C_4H_8O_2$, $C_{10}H_{14}N_2 \cdot 3C_{18}H_{34}O_2$ and $C_{10}H_{14}N_2 \cdot 3C_{18}H_{36}O_2$, respectively.

LITERATURE CITED

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LIQUID-VAPOR EQUILIBRIA IN THE BENZENE - CARBON TETRACHLORIDE SYSTEM. I*

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The benzene — carbon tetrachloride system is employed more often than others in determining the efficiency of rectifying columns. In this, the data of Rosanoff and Easley [1] on liquid-vapor equilibria in this system at the pressure of 760 mm are employed. These data are incomplete (the research was carried out in the interval of 5–72 mol.% of CCl_4), and, besides, we had reason to believe that they were not accurate enough.

The present research was undertaken with the object of checking and supplementing the Rosanoff and Easley [1] data.

Purity of the Substances and Methods of Analysis

Carbon Tetrachloride. The ordinary commercial product, distilled in a column (22 theoretical plates) was used.

The purified CCl_4 had the following constants:

	Ours	Rosanoff and Easley [1]	Grimm [2]
Boiling pt., 760 mm	76.69	76.69	76.71
d_4^{20}	1.5952		
n_D^{20}	1.46037	1.4603	1.4604

Benzene. Here too, the commercial product was used, washed with sulfuric acid and a solution of soda; the product freed from water was distilled in a column and frozen three times.

The benzene thus prepared possessed the following constants:

	Ours	Woiciechowski [3]	Richards and Hargreaves [4]	Rosanoff and Easley [1]
Boiling pt., 760 mm...	80.09	80.094	80.06	80.25
d_4^{20}	0.8788	0.87896		
n_D^{20}	1.50115	1.50122	1.5011	1.5009

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* Presented at the meeting of the Chemical Scientific Research Institute of Leningrad State University, October 15, 1947

Griswold and Bowden [5] suggested purifying benzene by azeotropic distillation with acetone. To benzene there are added 12% by volume of acetone, and the mixture is distilled in a column. The authors assume that the acetone would carry off the impurities. By means of this type of distillation, the authors, starting with benzene of n_D^{20} 1.4996, obtained benzene of n_D^{20} 1.5009.

We took benzene with n_D^{20} 1.5003 and, after "azeotropic" distillation in a column with 50 theoretical plates, we obtained benzene with n_D^{20} 1.5007. The same input benzene, washed with sulfuric acid and a soda solution and distilled in the same column without the addition of acetone, had a n_D^{20} 1.5009, and after the subsequent triple freezing, this value became n_D^{20} 1.50115. Thus, the purification of benzene with acetone is inferior to ordinary rectification: washing with sulfuric acid and a soda solution, driving off the water, and then freezing it.

Analysis of mixtures of benzene and carbon tetrachloride were made by specific gravity. For this purpose the specific gravities of the mixtures prepared were determined. The results of these determinations are listed in Table 1.

TABLE 1

Densities of Solutions of Benzene and Carbon Tetrachloride

Composition of prepared solutions (in mol.% of CCl_4)	d_4^{20}	Composition of solution, computed by linear equation	Correction
0.00	0.8788		
9.10	0.9484	9.72	- 0.62
18.43	1.0190	19.57	- 1.14
28.21	1.0922	29.79	- 1.58
37.99	1.1641	39.83	- 1.84
47.85	1.2362	49.90	- 2.05
58.00	1.3080	59.92	- 1.92
68.29	1.3801	69.99	- 1.70
78.53	1.4504	79.80	- 1.27
85.87	1.4999	86.71	- 0.84
94.54	1.5583	94.86	- 0.32
100.00	1.5952		

Calculation of concentrations according to specific gravities was done semi-analytically, semi-graphically, by the method due to Zawidski [6]. The solution concentration was computed from the specific gravity on the assumption that there is a straight-line relationship between specific gravity and concentration. The difference between concentrations thus calculated and the actual concentrations comprised the corrections (Column 4 in Table 1). These corrections were plotted against the computed concentrations. The mean deviation from the average value at the given concentrations was ± 0.03 mol. %.

Apparatus for Determining Liquid-Vapor Equilibria

Various apparata are described in the literature for determining liquid-vapor equilibria. Some of them were reproduced by us. Investigation of their work indicated that though they yielded fairly accurate results, they possessed one disadvantage or another. (We were able to judge the deficiencies of other apparata, untested by us, from the experience we had accumulated.) We therefore resolved to select one of the apparata tested by us, to eliminate the defects we had discovered, and thus to make it suitable for precision operation. The simplest and most convenient of the apparata tested by us was V.A. Kireyev's apparatus [7], (Fig 1).

This apparatus possesses considerable advantages over those described in foreign literature. It also has one deficiency, however: partial condensation of the vapor in the upper portion of the boiler As a result, the distillate is always somewhat richer in the more volatile constituent nowwithstanding the good insulation of this part of the apparatus. To prevent the partial condensation Kireyev heats the upper part of the boiler with an electric winding. This step eliminates the partial condensation, but then one can by no means rely on the correctness of the thermometer readings. Moreover, use of the electric heating coil complicates operation. We therefore resolved to try to eliminate the partial condensation otherwise. The apparatus with the changes made by us is shown in Fig. 2.

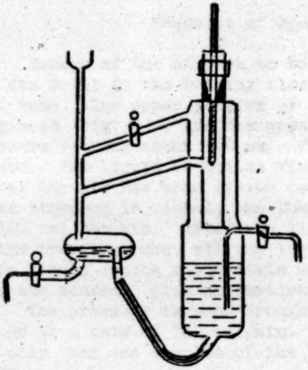

Fig. 1

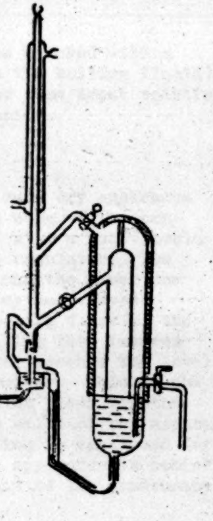

Fig. 2

The principal feature of this design is that the central tube is lengthened and lowered into the liquid As a result, the vapor reaches the distillate receiver without undergoing partial condensation, the latter being prevented by the heating of the internal tube by the vapors outside it. Thus the partial condensation is automatically eliminated.

The condensate receiver is likewise changed, compared to the receiver in the Kireyev apparatus. To attain equilibrium more rapidly, the tube carrying the condensate to the receiver is led almost to the bottom of the latter. A dropping tube is inserted to record the boiling rate. The tube carrying the condensate to the boiling flask is of the same design as in Kireyev's apparatus This feature, besides the good intermixing of the condensate with the boiling liquid it affords, as noted by him, is also very important in still another respect: it prevents over-heating (at normal pressure or somewhat reduced pressure) and makes it possible to effect boiling at any desired rate. There is no thermometer in our apparatus. We removed it, on the one hand, to eliminate partial condensation on it, and on the other, because, situated as it was in the vapor phase it could never give a fully accurate boiling temperature. We used Swentoslawski's ebulliometer [8] to measure accurate boiling temperatures.

The precision of operation of the apparatus described was checked with a mixture of benzene, [illegible] carbon tetrachloride (40 mol.% of CCl_4 in the boiling liquid). The deviations of the results obtained in repeated tests of the same input solution at different boiling rates did not exceed the error of observation.

Sequence of Operations with the Apparatus

Enough of the mixture to be tested is poured into the clean, dry apparatus for its level in the boiling flask to be 1 cm above the bottom edge of the central tube. The upper portion of the boiling flask was covered with a heat-insulating hood (Fig. 2), and the apparatus connected to a pressure regulator. The pressure set was about 760 mm. The upper stopcock is opened, and the lower one closed. The liquid is boiled vigorously. Then, after some time has elapsed (after the air has been driven out of the upper part of the boiling flask), the upper stopcock is closed, the lower one is opened, and the boiling rate lowered to 100 cal per min. After the liquid in the condensate receiver reaches the level of the overflow tube, all the liquid is drained out of the receiver. This is the waste liquid (which may contain water driven off from the boiling flask together with the benzene plus impurities that may have adhered to the walls of the apparatus. The pressure is then brought to exactly 760 mm and boiling is continued for 1 hour at a rate of 100 cal/min.* After boiling is ended, the apparatus is cooled, and only then are samples of the liquid in the boiling flask and of the condensate taken.

Results of Investigating Liquid-Vapor Equilibria and Checkup Methods

The results obtained with the apparatus described above are given in Table 2.

Plotting the data of this table in a diagram (boiling temperature, liquid and vapor composition) together with Rosanoff's and Easley's data shows that both sets are in good agreement. Rosanoff and Easley carried their research only as far as 72 mol.% of CCl_4, whereas we went as high as 96%. Thus, we were unable to check our results for the concentrations above 72% by comparing them with those obtained by other authors; the fact that our points coincided satisfactorily with extrapolated curves was no indication of their correctness. (In such cases the check is usually made by means of the Duhem-Margules equation). This method of verification takes considerable time. Moreover, when it is used for checking isobar data, one must know the variation of the boiling temperature with composition and the variation of the vapor tension of the pure constituents with temperature over the range extending from the boiling point of the less volatile constituent to the boiling point of the more volatile constituent for the given pressure. Frequently such data are not available in the literature.

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* As operation of the apparatus has shown, the composition of the liquid in the condenser reaches a state of equilibrium 30 minutes after collection of the condensate is begun, but for the sake of accuracy we continued boiling for another 30 minutes.

Table 2

Liquid-Vapor Equilibria in the $C_6H_6 - CCl_4$ System; $P = 760$ mm.

d_4^{20}		Composition in mol.% CCl_4		α
Liquid	Vapor	Liquid	Vapor	
0.9209	0.9279	5.51	6.43	1.182
1.0516	1.0719	22.76	25.48	1.159
1.1203	1.1406	32.02	34.78	1.132
1.1924	1.2138	41.87	44.82	1.128
1.1955	1.2159	42.29	45.09	1.120
1.2629	1.2793	51.63	53.93	1.097
1.3174	1.3308	59.33	61.23	1.082
1.3771	1.3869	67.87	69.28	1.068
1.4165	1.4234	73.58	74.62	1.056
1.4673	1.4707	81.02	81.52	1.037
1.4953	1.4980	85.19	85.60	1.033
1.5247	1.5262	89.55	89.78	1.025
1.5586	1.5590	94.59	94.66	1.014
1.5713	1.5713	96.42	96.42	

We therefore determined to try to use the function α (relative volatility) as a check.

The composition of the liquid and the composition of the vapor are related as we know by the following equation:

$$\frac{y}{100 - y} = \alpha \frac{x}{100 - x} \qquad (1)$$

where y and x are the molar percentages of the more volatile constituent in the vapor and in the solution, respectively, and α is the relative volatility; in the general case, α is a function of x.

If we substitute experimentally determined values of x and y in the foregoing equation, compute the corresponding value of α, and then plot the curve of α versus x, the values of α will lie on a smooth curve if the experimental data are reliable.

At the present time the (α, x) diagram is fairly widely used to compute the efficiency of laboratory rectifying columns and for other calculations in the field of rectification. In these computations the mean value of α in the given concentration [illegible] is used. The (α, x) diagram is hardly employed at all to check the correctness of experimental data on liquid-vapor equilibria. Strictly speaking, it is sometimes cited, but in passing, as it were, without discussing it in detail, drawing no conclusions therefrom and making no use of it to correct wrong data; this method is highly accurate and very simple, however. It is suitable for checking data obtained under isobaric as well as isothermal conditions. The results were found to be highly interesting.

The checkup method involving the Duhem-Margules equation is the classic one. It might be thought that the checkup method involving the (α, x) diagram is not employed because it can be used only to judge the incorrectness of individual tests, it being useless in determining the correctness of the whole liquid-vapor equilibrium curve. To clear up this problem we compared a checkup using the Duhem-Margules equation made by Beatty and Callingaert [9] with our checkup using the (α, x) diagram. The results of this comparison are listed in Table 3.

This comparison shows that the checkup methods using the Duhem-Margules equation and the (α, x) diagram yield identical results, on the whole. But the results obtained from the (α, x) diagram are more detailed; they subdivide the liquid vapor equilibrium curve into more or less reliable sections.

In the general case one deficiency of the checkup method using the (α, x) diagram is its extraordinary sensitivity at very low and very high concentrations of one constituent. When the literature data are checked by this method, the scattering of points obtained on the (α, x) diagram by this method is so great at low and high temperatures that checking the line $\alpha = f(x)$ becomes impossible. (This check would have been possible had the authors given a larger number of points for these areas, but they usually cite fewer points for these areas than for the middle concentrations.)

In the cases cited, we simply have to discard the data for the extreme regions of the (α, x) diagram, *e.g.*, to consider that the data are correct over the range of 5-90% of the volatile constitutent. When one is checking his own data and it becomes necessary, for one reason or another, to know the outer areas of the (α, x) diagram, repeated determinations of the liquid-vapor equilibria in these areas must be made. In such cases the method of determining liquid-vapor equilibria in a column is extremely useful. Sometimes the increased sensitivity of the checkup method based on the (α, x) diagram at the ends of the curve is of advantage when investigating the location of azeotropic curves and the liquid-vapor equilibria in their vicinity. This investigation must be made in a rectifying column.

Increased sensitivity in the region of low and high concentrations exists even when checked by means of the Duhem-Margules equation, but it is then less pronounced.

The values of α computed from our data are listed in Table 2 and are plotted against the corresponding values of x in Fig. 3.

The circles in Fig. 3 denote the values of α computed from our data; the crosses denote the values computed from the data of Rosanoff and Easley [1]. (The values of α for values of x above 95% will be dealt with below.) As the figure indicates, the values of α as computed from our data and the data of Rosanoff and Easley are grouped about a straight line; the minor scattering of the points is due to the high sensitivity of this checking method.

The plotted straight line may be represented by the following equation:

$$\alpha = 1.203 - 0.00203\, x. \qquad (2)$$

Table 3

Comparison of Our Conclusions in Checking Literature Data on Liquid-Vapor Equilibria by Means of the $(\alpha, \underline{x})$ Diagram with the Conclusions of Beatty and Callingaert in Checking by Means of the Duhem-Margules Equation

System	Our Conclusions	Beatty's and Callingaert's Conclusions
Toluene-*n*-octane (isobaric data) Bromley and Quiggle [10]	Extremely poor data. Course of $\alpha = \underline{f}(\underline{x})$ is an incorrect wavy line. The section of the curve from 48 to 91 mol.% of toluene is acceptable. Here the overwhelming majority of the curves lie on a straight line. The data for concentrations outside this range are unreliable.	"Preliminary research leads to the conclusion of considerable inaccuracy...In general, there is no chance of correcting this material."
n-heptane—toluene (isobaric data) Bromley and Quiggle [10]	First impression that these data are better than those above. More detailed study indicates that the curve has some sort of unnatural discontinuity at middling concentrations. This break can be smoothed out, but then the course of the curve is not entirely borne out by the experimental data. As a result, the data are acceptable as approximate in the range of 25-83 mol.% of *n*-heptane. The data are wholly unreliable at concentrations below 25%. There are no experimental data above 88%.	"Preliminary research indicated that the data are acceptable. Calculation, made by graphic integration, led to the conclusion that the data are inaccurate."
n-hexane-benzene (isobaric data) Tongberg and Johnston [11]	Fully reliable data in the range of 4-80 mol.% of n-hexane. Data outside this range unreliable, particularly in the 0-4% interval.	"Sufficiently accurate data."

Table 4

Liquid—Vapor Equilibria in the C_6H_6—CCl_4 System, [illegible] $\alpha = \underline{f}(\underline{x})$, Computed from the Diagram

Corrected Data for the Liquid—Vapor Equilibria

x mol.% CCl_4	α	y mol.% CCl_4	x mol.% CCl_4	α	y mol.% CCl_4
5	1.193	5.91	55	1.091	57.14
10	1.183	11.62	60	1.081	61.85
15	1.173	17.14	65	1.071	66.55
20	1.163	22.52	70	1.061	71.23
25	1.152	27.74	75	1.051	75.92
30	1.142	32.86	80	1.041	80.63
35	1.131	37.85	85	1.031	85.38
40	1.121	42.77	90	1.020	90.18
45	1.111	47.62	95	1.010	95.05
50	1.101	52.40			

We computed the values of α for $\underline{x}$ = 5, 10, etc. molar percentages of CCl_4 in the solution. The corresponding values of $\underline{y}$ were then computed from these values of α.

We thus obtained corrected data for the liquid-vapor equilibria. The results are seen in Table 4.

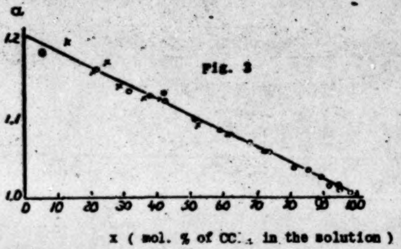
Fig. 3

Determination of the Boiling Point

The boiling point of the solutions was determined by means of Swentoslawski's ebulliometer [8]. The ebulliometer was connected to the pressure-controlling apparatus. The temperature was read off on a thermometer so chosen that the mercury meniscus did not protrude from the apparatus at all readings. We carefully calibrated the thermometer against a Baudin thermometer. It could be read with an accuracy of $\pm$ 0.01°. The pressure was kept constant within $\pm$ 0.1 mm Hg.

The results are tabulated in Table 5.

Table 5

Boiling Points of C_6H_6 – CCl_4 Solutions at $\underline{P}$ = 760 mm

Molar % CCl_4 in solution	Boiling point °C	Molar % CCl_4 in solution	Boiling point °C
0.00	80.09	73.38	76.92
4.55	79.76	78.10	76.83
9.25	79.42	83.89	76.78
13.92	79.14	89.14	76.74
23.36	78.63	91.50	76.73
33.04	78.13	93.58	76.72
47.83	77.56	95.90	76.71
57.94	77.26	97.78	76.70
68.01	77.02	100	76.69

Search for an Azeotrope

In the American literature we encounter the conviction that the benzene – carbon tetrachloride system has an azeotrope at 760 mm Hg consisting of about 95 molar % of CCl_4. In 1929, Grimm [2], while studying the variation of the boiling point with composition at 720 mm, proved that this system has no azeotrope at this pressure and expressed the opinion that it occurs at lower pressures.

Grimm's work remained unnoticed; down to the present we come across the assertions in American publications that there is an azeotropic mixture at 760 mm.

The only moot point is its precise composition.*

The data given above in Table 5 indicate that at 760 mm the boiling point rises linearly as the benzene concentration is raised and that no azeotrope is present. We resolved to continue this investigation -- to learn whether there is any azeotrope in this system at all, and at what pressures it is manifested.

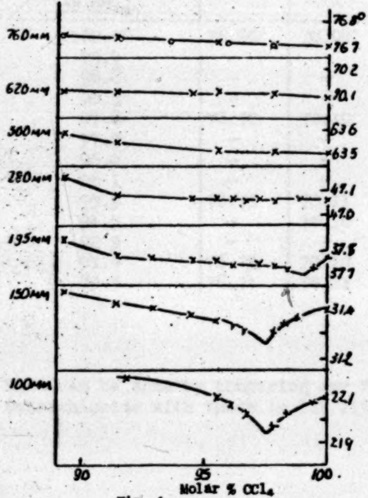

Fig. 4

To do this we made use of the same Swentoslawski instrument. With it we traced the variation of the boiling point with composition in the range of 89-100 molar % CCl_4 at pressures of 760, 629, 500, 280, 195, 150, and 100 mm Hg. The choice of these pressures was governed by the choice of thermometers available to us that met the proviso that the mercury meniscus should not protrude from the apparatus.

The thermometers were calibrated against the Baudin thermometer. Pressures were read on a mirror scale and a cathetometer. For our computations we employed only the cathetometer indications. The readings on the mirror scale served for setting the pressure initially and as a control. Temperatures were read to ± 0.01°, and pressures to ± 0.1 mm Hg.

Owing to the fact that it was difficult to obtain the exact pressure required, we determined the boiling point at 3 to 4 mm pressure above and below the required pressure; for example, 192.1, 193.2, 194.8, 197.0, 200.0, and 197.8 mm, and then found the boiling point at the required pressure (195 mm in this case) by interpolation from a graph. This eliminated accidental errors in individual tests.

The data obtained are listed in Table 6 and shown in Fig. 4.

Circles and crosses are plotted along the top straight line. The circles represent the data of Table 5, and the crosses those of Table 6. The figure demonstrates that an azeotrope is exhibited in the C_6H_6–CCl_4 system at pressures below 280 mm (below 47°). At the pressure of 100 mm the azeotrope has ~97.6 molar % of CCl_4 and boils at ~21.95°.

These figures may be looked upon as relatively accurate. To ascertain the presence of an azeotrope, we had to get merely the course of the curves. It was also of interest, however, to determine the absolute accuracy of these figures.

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* In Herschell and Hunt's manual of physical chemistry the (y,x) diagram is given for the C_6H_6--CCl_4 system, with the azeotrope shown at 85% by weight of CCl_4 at 760 mm. of Hg.

Table 6

Variation of Boiling Point with Composition of C_6H_6 – CCl_4 at Various Pressures

P / Solution Composition in Molar % of CCl_4	P 760	620	500	280	195	150	100 mm
100.0°	76.69°	70.08°	63.50°	47.06°	37.77°	31.40°	22.09°
99.4	–	–	–	–	37.73	–	22.07
98.8	–	–	–	47.07	–	31.37	–
98.3	–	–	–	–	37.72	31.34	22.02
97.8	76.70	70.10	63.51	47.05	37.73	31.32	21.97
97.2	–	–	–	47.06	37.74	–	–
96.6	–	–	–	47.05	–	31.31	22.02
96.1	–	–	–	47.06	37.73	31.33	22.06
95.5	76.71	70.11	63.51	47.06	37.75	31.35	22.09
94.5	–	70.10	–	47.06	37.75	31.37	
92.9	–	–	–	–	37.77	31.40	22.17
91.4	76.73	70.10	63.54	47.07	37.77	31.42	–
89.3	76.74	70.11	63.58	47.15	37.84	31.47	–

This can be done by comparing our figures for the boiling point of pure carbon tetrachloride with those in the literature. This comparison is made in Table 7.

Table 7

Comparison of our Data on the Boiling Point of CCl_4 with Those in The Literature Recomputed for Our Pressures

P / data	P 760	620	500	280	195	150	100 mm
Ours	76.69°	70.08°	63.50°	47.06°	37.77°	31.40°	22.09°
Scatch [13].	76.69	70.00	63.60	47.00	37.70	31.40	–
Perry [14]. . . .	–	70.09	63.00	47.10	37.90	31.50	22.20

The boiling points for CCl_4 obtained by Scatchard and Perry were interpolated by us to get figures for our pressures.

Liquid-Vapor Equilibria at CCl_4 Concentrations of 90-100 Molar %

In Table 2 there are given data for the liquid-vapor equilibria determined in the apparatus of Fig. 2 (referred to henceforth as the single-evaporation apparatus), pushed as high as 96.42 molar % of CCl_4 in the liquid.

Determining equilibria at high concentrations was impossible with this method, because the composition of the vapor was too close to that of the liquid; that is why the last line of Table 2 should be taken to mean that the difference between the composition of the vapor and that of the liquid was less than the observational error. To investigate equilibria at this and even higher concentrations of CCl_4 in the liquid, some other method would evidently have to be employed.

This research was of interest in that it would make it possible to give a definitive answer to the problem of the presence or absence of an azeotrope in this system at 760 mm. Moreover, it was of some interest to trace the variation of α with $\underline{x}$ up to 100%.

We decided to try out the following method for this investigation. In a rectifying column, operating by itself (without separation), the composition of the vapor condensed in the dephlegmator and that of the liquid in the still are related to each other by the following equation:

$$\frac{y'}{100 - y'} = \alpha^n \frac{x'}{100 - x'} \tag{3}$$

where $\underline{y}'$ and $\underline{x}'$ are the molar percentages of the volatile constituent in the dephlegmator and in the still, respectively, α is the relative volatility, and $\underline{n}$ is the number of stages or number of evaporations in the column (in general, the number of theoretical plates without allowing for the plate corresponding to the transition still-column).

As will be shown in the next article, a modern column may be operated with high accuracy. The number $\underline{n}$ is obtained with good repeatability when the column's efficiency is determined in repeated experiments. Moreover, it will likewise be shown that, contrary to the opinion prevailing in the literature, the efficiency ($\underline{n}$) is independent of the liquid concentration in the still.

That is why a modern column may be employed as an apparatus for determining liquid-vapor equilibria. In the column the process of evaporation and condensation is repeated $\underline{n}$ times. Hence, the difference in the composition of the vapor and the liquid, which does not yield to analysis in single evaporation is multiplied, roughly speaking, $\underline{n}$ times when a column is used. It may be said that a single-stage evaporation instrument is to a column as the naked eye is to a microscope.

The method involving the use of a column to determine liquid-vapor equilibria is as follows: at first the number $\underline{n}$ is determined by repeated careful tests. To do this a solution is poured into the still of such a composition as to enable the computation of $\underline{n}$ from the (y,x) diagram; i.e., $\underline{n}$ is determined from the data obtained in the apparatus for single-stage evaporation. The liquid in the still is then replaced by a solution with a high concentration of the more volatile constituent. The column, working by itself, is brought to equilibrium, and samples of the liquid are taken from the dephlegmator and analyzed. The data obtained are substituted in Equation (3) together with the value of $\underline{n}$ previously determined. This enables us to compute α. Evidently, this is the mean value of α; it represents a liquid composition $x = \frac{y' + x'}{2}$. Substituting the values of α and $\underline{x}$ thus found in Equation (1), we find $\underline{y}$, the composition of the vapor in equilibrium with the liquid of composition $\underline{x}$ during single-stage evaporation. We used for this purpose a column 1.5 cm. in diameter with multiple separation. All runs began with complete, uniform wetting of the nozzle. The rate at which the reflux was returned from the dephlegmator was 200 drops/min. The solution composition was determined, as before, by the specific gravities.

The results of the tests are given in Table 8.

Table 8

Liquid-Vapor Equilibria in the $C_6H_6 - CCl_4$ System Determined by the Rectifying Column

$\underline{x}'$ Composition of liquid in still Mol.% CCl_4	$\underline{y}'$ Composition of vapor in dephlegmator. Mol.% CCl_4	α Experimental	α On extrapolated straight line	Liquid-Vapor equilibria		
				$x = \frac{y' + x'}{2}$	y computed from experimental α	y computed from extrapolated α
6.25	70.03	1.126	1.126	38.14	40.97	40.97
84.40	90.81	1.020	1.025	87.60	87.81	87.86
91.64	94.21	1.013	1.014	92.92	93.01	93.01
94.75	95.79	1.008	1.010	95.27	95.31	95.32
97.96	98.19	1.004	1.004	98.07	98.08	98.08
99.40	99.43	1.002	1.001	99.41	99.41	99.41
99.44	99.45	1.001	1.001	99.44	99.44	99.44

Six tests were run to determine the value of $\underline{n}$, with a concentration of 6.3 mol.% CCl_4 in the still and 70.00 mol. % in the dephlegmator.

The mean value of $\underline{n}$ was 30 stages (theoretical plates). In the seventh test we did not compute $\underline{n}$, but took the value of $\underline{n}$ as 30 and computed α. The data of this test are listed in the first line of the table. The second line gives the figures of another single test. The data of all the other lines represent the means of 3 to 5 repeated tests.

Table 8 shows that the $C_6H_6 - CCl_4$ does not possess an azeotrope at 760 mm and that the straight-line variation of α with $\underline{x}$ continues up to 99.5 molar % CCl_4. An indispensable condition for the success of this method is the repeated "discards" at the beginning of the column's operation. At the beginning of operation of the column, volatile impurities (and in the present system water as well) which are present in such negligible amounts in the ingredients of the mixture as not to produce any appreciable effect upon the physical-chemical constants of these ingredients, are accumulated in the upper portions of the column. These ingredients have to be eliminated, discarded. This is done by bringing the column to a state of equilibrium, after which the bottoms accumulated in the dephlegmator are thrown away. These discards are repeated several times.

The results listed in Table 8 are not of any appreciable interest. The fact that the system has no azeotrope was quite evident from our investigation of the boiling point. The fact that α continues to be a linear function of $\underline{x}$ up to 99.5 molar % of CCl_4 is of somewhat greater interest. We employed this method not so much to obtain the indicated results as to ascertain the feasibility of this method and its precision in the case of such a simple system. As the results obtained indicate, the method turned out to be fully satisfactory. Our most recent work demonstrated that this method is irreplaceable in the following cases:

1. When α is close to unity (single-stage evaporation apparata cannot be used) and its variation with $\underline{x}$ is not suitable for extrapolation and interpolation. In these cases we must have available an accurate method of analysis or a column with a high value of $\underline{n}$; a particularly precise equilibrium setting within the column need not be striven for;

2. When the difference between the compositions of the vapor and the liquid in single-stage evaporation are not very small, but the method of analysis is so inaccurate that the data obtained with the single-stage evaporation apparatus cannot be trusted; here we must strive for the establishment of equilibrium with special care, since in these cases α varies widely with $\underline{n}$.

CONCLUSIONS

1. The liquid-vapor equilibria in the C_6H_6–CCl_4 system at 760 mm Hg in the range from 5 to 95 molar % of CCl_4 were investigated. This research corroborated the correctness of Rosanoff's and Easley's data and supplemented them.

2. A device was constructed to determine liquid-vapor equilibria, representing a change in the instrument designed by V.A.Kireyev.

3. The (α,$\underline{x}$) diagram was employed to check the correctness of the experimental data on liquid-vapor equilibria. This method of checking is accurate and simple, and suitable for checking isobaric and isothermal data.

4. The variation of the boiling point with composition in the C_6H_6–CCl_4 system was investigated over the range 0-100% at a pressure of 760 mm and over the range of 89-100 molar percent of CCl_4 at pressures of 760, 620, 500, 280, 190, 150, and 100 mm of Hg.

It was learned that in this system an azeotrope is exhibited at pressures below 280 mm (below 47°). At a pressure of 100 mm the azeotrope has a composition of about 97.6 molar per cent and boils at about 21.93°.

5. A new method for determining liquid-vapor equilibria in the rectifying column has been suggested and tested. This method was evaluated for cases in which the difference between the vapor and liquid compositions is small or the method of analysis is not accurate enough.

This method was used to study the liquid-vapor equilibrium in the C_6H_6–CCl_4 system over the range form 90 to 99.5% CCl_4.

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THE CHROMATOGRAPHY OF IONS

I. THE THEORY OF CHROMATOMETRY

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The problem of the relationship between the length of a zone in a chromatogram and the amount of adsorbed substance was first raised by M.S.Tsvet. We cite a passage from M.S. Tsvet's work [1]: "The question now arises whether the chromatographic method cannot be used as a chromatometric one. The possibility of expressing the quantity of pigments simply by the volume of adsorbent with which it is saturated was very attractive. Experiments I made along this line, however, have not yielded any satisfactory results up to now. Owing to the interaction of the deposited pigments the colored zones do not achieve an identical degree of saturation."

Thus, the problem of the possibility of quantitatively determining the chromatographed substance by the length of the zone it forms in the chromatogram (chromatometry) was initially posed by M.S. Tsvet. It is evident from the foregoing quotation that although M.S.Tsvet studied this problem, he found no solution in his work.

The relationship between the concentrations of the solute and the length of the zone in the exchange-ion chromatogram was the subject of research by Schwab and Dattler [2]. They took as a permutent* alumina, as suggested by Brockman. Using as their examples the pair of Cu^{+2} and Co^{+2} ions, these authors showed that there is an approximate correspondence between the ratio of the zone lengths of both ions and the ratio of the ion concentrations in the initial solution.

The length of the cation zone in the chromatogram, however, does not depend on the cation concentration alone, but also on that of the corresponding anion, provided the valency of the cation is greater than unity. In this case secondary adsorption of the anion is always possible. The normal exchange of the univalent M^+ and the bivalent M^{+2} cations is given by the following:

$$(Al_2O_3)_{\underline{\underline{m}}}AlO_2^- \; Na^+ + MZ \rightleftarrows (Al_2O_3)_{\underline{\underline{m}}}AlO_2^- \; M^{++} + NaZ \qquad (a)$$

$$(Al_2O_3)_{\underline{\underline{m}}}\begin{matrix} AlO_2^- \; Na^+ \\ AlO_2^- \; Na^+ \end{matrix} + MZ_2 \rightleftarrows (Al_2O_3)_{\underline{\underline{m}}}\begin{matrix} AlO_2^- \\ AlO_2^- \end{matrix} M^{++} + 2NaZ \qquad (b)$$

The secondary adsorption of the Z^- anion is given by the following equation:

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* We call adsorbents that are suitable for ion exchange "permutents" [3].

$$(Al_2O_3)_{\underline{m}}AlO_2^- \,\vdots\, Na^+ + MZ_2 \rightleftarrows (Al_2O_2)_{\underline{m}}AlO_2^- \,\vdots\, M^{++}Z^- + NaZ \qquad (c)$$

The foregoing equations show that secondary adsorption of anions is impossible when the adsorbing cation is univalent. Secondary adsorption of anions has as its result that when chromatograms are formed by univalent and bivalent cations (such as Cu^{+2} and Ag^+ from a solution of nitrates) zones of identical length are formed in equi-atomic rather than equivalent quantities. This is due to the fact that in the chromatogram the Ag^+ ion is adsorbed via mechanism "a", while the Cu^{+2} ion is adsorbed in accordance with mechanism "b". When chromatograms are formed from an ammoniacal solution, the zones produced are longer than in those from aqueous solutions. The lengthening of the zone is caused by the fact that NH_4^+ ions compete with the Cu^{+2} ions in exchanging with the Na^+ ion.

Schwab and Dattler cite two analyses of brass and coin metal by the chromatographic method. In fact, the chromatographic method may be employed quantitatively for copper, as Cu^{+2} is strongly adsorbed on basic aluminum oxide. Chromatometry will not yield satisfactory results for ions that are poorly adsorbed.

2. Linear Absorptive Capacity of a Permutent

In chromatography the concept of the linear absorption capacity $\underline{Q}$ is very important In exchange-ion chromatography the linear absorption capacity $\underline{Q}$ is expressed in mg eq of the exchange ion per cm of length of column of the permutent. We introduce the following notation:

L_o = length of the permutent column (in cm).

g = weight of the permutent column (in g).

$S_{\underline{m}}$ = absorption capacity of the permutent, i.e. the quantity of the exchange ion (in mg equivalents) per gram of permutent.

In these terms the linear absorption capacity is expressed thus:

$$\underline{Q} = \frac{gS_{\underline{m}}}{L_o} \; \frac{\text{mg eq.}}{\text{cm}} . \qquad (1)$$

It is evident that the linear absorption capacity depends on the diameter of the column $\underline{d}$ in cm (or on the internal diameter of the tube filled with the permutent) and on the bulk weight of the permutent $\underline{W}$ in g/mol. The area of filtration will be $\pi d^2/4$ sq cm; hence the linear absorption capacity may be expressed as follows:

$$\underline{Q} = \frac{\pi d^2 W S_{\underline{m}}}{4} = AWS_{\underline{m}} \; \frac{\text{mg eq.}}{\text{cm}} \qquad (2)$$

3. Plan of an Ideal Exchange-Ion Chromatogram

In chromatometry the determination of the maximum zone length for a given ion in the exchange-ion chromatogram is extremely important. In computing the minimum zone length the concept of the ideal exchange-ion chromatogram is extremely useful. The plan of an ideal chromatogram is as follows: 1. every zone of the chromatogram contains only one ion in the adsorbed state; 2. The liquid in the pores of the permutent contains no ions of the initial solution. For, let the permutent be XM_1 and the solution M_2Z, M_3Z,..., the ion concentrations for M_1, M_2,...$M_{\underline{i}}$ being $\underline{c_1^{\circ}}$, $\underline{c_2^{\circ}}$,...$c_{\underline{i}}^{\circ}$. Through the permutent column there are passed $\underline{v}$ ml of the solution of mixed salts. In the ideal chromatogram the zone length of each $\underline{i}$ ion, λ°, is determined by the following equation:

$$\lambda_{\underline{i}}^{\circ} = \frac{\underline{v}c_{\underline{i}}^{\circ}}{Q} \text{ cm.} \tag{3}$$

And this will be the minimum possible zone length in the chromatogram for a pure exchange of ions M_2, M_3, etc., for the ion M_1, uncomplicated by the secondary adsorption of Z ions.

In the actual exchange-ion chromatogram the zones are not pure, and therefore in actuality we must expect that the zone length, λ, in actual chromatograms, must deviate somewhat from the minimum value λ°; it is obvious that $\lambda^{\circ} < \lambda$.

Comparison of the zone length found experimentally with the minimum zone length provides a semiquantitative characteristic of the adsorption distribution of the ions in the column without a detailed quantitative analysis of the composition of the permutent and solution equilibria, which is often impossible in practice (owing to the displacement of the adsorption equilibrium when the equilibrium solution is removed from the permutent).

At the present time the variation of the zone length with the number of ions introduced has been investigated for the $Cu^{+2} - Co^{+2}$ chromatogram.

4. Notes on Method

In our tests we made use of permutite, investigated in our preceding researches [3,4].

The technique of producing a chromatogram has been described already [3]. The permutite, in the form of dry powder, was placed in a glass tube open at the bottom. The grain size was about 0.1 mm.

5. Variation of Zone Length in a Chromatogram with the Volume of Solution Introduced, Solution Concentration Being Kept Constant

Let us now describe the tests performed to elucidate the equation $\lambda = \underline{f}(v)$ for constant solution concentrations.

In Experiment 1 we studied the change in zone length as a solution of definite concentration is added, i.e., the function $\lambda = \underline{f}(\underline{v})$. Column data for this test:

$g = 0.782$ g, $L_0 = 4.0$ cm, $\underline{d} = 0.7$ cm, $A = 0.385$ sq. cm., $W = 0.51$ g/ml, $S_{\underline{m}} = 2.30$ mg eq/g, $Q = 0.45$ mg eq/cm. Solution used: a 1:1 mixture of N/10 $CuCl_2$ and N/10 $Co(NO_3)_2$.

The solution was poured into the column in individual 1-ml batches. When the first milliliter of solution was added, the length of the blue zone was 0.25 cm, and that of the pink zone was 0.5 cm. Then 3 cm of the column was wetted with a colorless solution of sodium salts. When the second milliliter of solution was added, the zone lengths were 0.4 and 0.9 cm, respectively; the colorless solution began to flow out of the column. The results are plotted in Fig. 1. In all 10 separate milliliter batches of solution were poured in The filtrate flowing out was colorless and contained neither copper nor cobalt. The values of $\underline{v}$ are plotted on the axis of abscissas, from 1 to 10; the ordinates are the zone length λ (in cm). For Cu^{+2}, beginning at $\underline{v} = 1$ ml, and Co^{+2}, beginning at $\underline{v} = 4$ ml, the zone lengths increase linearly with solution volume:

$$\left.\begin{array}{l}\text{For the } Cu^{+2} \text{ zones} \ldots \lambda_1 = 0.15\underline{v} + 0.1 \\ \text{For the } Co^{+2} \text{ zones} \ldots\ldots \lambda_2 = 0.20\underline{v} + 0.5\end{array}\right\} \quad (4)$$

In the ideal chromatogram the variation of λ with $\underline{v}$ ought to be of the form:

$$\lambda^0 = \frac{c^0}{Q} \cdot \underline{v} \qquad (5)$$

in accordance with equation (3), $\underline{c}^0$ being constant.

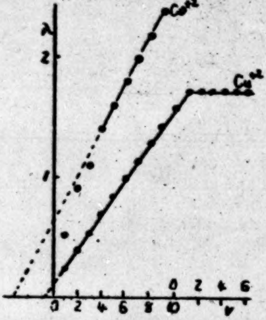

Fig. 1. Variation in zone length in the chromatogram Cu^{+2} -- Co^{+2} with volume of solution [N/20 $CuCl_2$, N/20 $Co(NO_3)_2$]

In our experiment, $\underline{c}^0/Q$ is 0.11 per sq cm; as Equation (4) indicates, the experimental coefficients of $\underline{v}$ are greater in this chromatogram than in the ideal case. After 10 ml of solution are added, the copper zone in the upper region is bluer and clearer in color than the lower region, where the color is purplish. This is apparently a transition zone, where Cu^{+2} and Co^{+2} are mixed The pink cobalt zone fills the column all the way to the end, the first drop of the filtrate being pinkish. It follows from Equation (4) that for $\underline{v} = 10$ ml, $\lambda_1 + \lambda_2 = 4.1$ cm. As the length of the column is 4 cm, cobalt appears in the filtrate after 10 ml of solution has been poured in. After the addition of the 10 ml of solution the chromatogram was washed with water in single 1-ml portions. In Fig. 1 the amount of water used is shown above the abscissas axis. When the first milliliter of water is added, the pinkish solution of cobalt salt begins to flow out. At the top the copper zone clears up to a pure blue color; lower down, from about the middle of the zone, the tone is lilac. The length of the sky-blue zone is 1.75 cm After the second milliliter of water is added, the solution that flows out is nearly colorless, while the length of the blue zone remains unchanged, and the sky-blue color clears up in the lower portion of the copper zone as well. The picture remains unchanged as washing is continued; the washing was stopped after the sixth milliliter. Thus, 0.5 mg/eq of Cu^{+2} forms a zone 1.75 cm long in the permutite column. The ideal zone length is $\lambda^0 = 1.11$ cm. Hence, it follows that the blue copper zone cannot be pure; it evidently contains some sodium.

Characteristics of the column in Experiment 2: $\underline{g} = 0.689$ g, $\underline{L}_0 = 3.6$ cm, $\underline{d} = 0.6$ cm, $\underline{A} = 0.283$ sq cm, $\underline{W} = 0.676$ g/ml, $\underline{S}_m = 2.30$ mg eq/g, $\underline{Q} = 0.440$ mg eq/cm. Solution used: a 1:3 mixture of N/10 $CuCl_2$ and N/10 $Co(CO_3)_2$.

10 ml of solution was passed through the column in 1 ml batches, i.e.,

0.25 mg/eq of Cu^{+2} and 0.75 mg eq of Co^{+2}.

The results obtained are shown in Fig. 2. The blue copper zone has a lilac tint at the bottom. The colorless filtrate flows out up to $\underline{v} = 9$ ml. At $\underline{v} = 9$ ml the filtrate that flows out begins to be pinkish in color. When the column is washed with water, the copper zone does not grow wider, its sky-blue color merely growing clearer. The function $\lambda = \underline{f}(\underline{v})$ looks like this:

$$\left.\begin{array}{ll} \text{For the } Cu^{+2} \text{ zone ......} & \lambda_1 = 0.1 \\ \text{For the } Co^{+2} \text{ zone ......} & \lambda_2 = 0.4\,\underline{v} + 0.1 \end{array}\right\} \quad (6)$$

In this test $\underline{c}^0/\underline{Q}$ equals 0.057 sq cm for Cu^{+2} and 0.17 sq cm for Co^{+2}. Hence, the sky-blue and pink zones are nearly twice as long as in the ideal chromatogram. It is evident that each zone contains the sodium ion in addition to the corresponding cation.

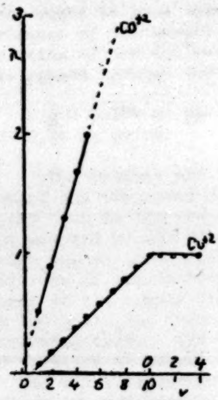

Fig. 2. Variation of zone length in the Cu^{+2} - Co^{+2} chromatogram with amount of solution [N/40 $CuCl_2$, 0.075N $Co(NO_3)_2$]

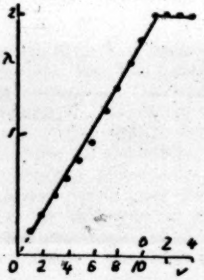

Fig.3. Length of the Cu^{+2} zone as a function of the volume of N/20 $CuCl_2$.

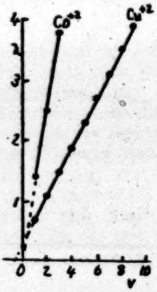

Fig. 4. Variations in zone length in the Cu^{+2} -- Co^{+2} chromatogram with amount of solution [N/20 $CuCl_2$, N/20 $Co(NO_3)_2$ and N/1 NaCl].

The incomplete expulsion of the sodium ion from the permutite may be demonstrated by the following tests. In Experiment 3 we studied the length of the copper zone in the permutite when N/20 $CuCl_2$ percolates down. The column characteristics were:

$\underline{g}$ = 0.548 g, $\underline{L}_o$ = 3.8 cm, $\underline{A}$ = 0.385 sq cm, $\underline{W}$ = 0.374 g/ml, $S_{\underline{m}}$ = 2.30 mg eq/g, $\underline{Q}$ = 0.33 mg eq/cm.

The solution, 10 ml, was poured into the column 1 ml at a time. Then the column was washed with water. The results are shown in Fig. 3. The equation of the straight lines is as follows:

$$\lambda_1 = 0.18\underline{v}. \tag{7}$$

After 10 ml of solution has been poured in, λ_1 = 1.8 cm. After 1 ml of water has been used for washing, λ_1 = 2.0 cm; the zone length does not change as the washing with water is continued. In this test $\underline{c}^o/\underline{Q}$ = 0.15 per sq cm. Therefore, the copper zone in the chromatogram is 1.2 times as long as the zone consisting entirely of copper permutite. Hence, the copper zone consists of a mixture of copper and sodium permutites.

If a sodium salt is introduced into the solution from the beginning, the zone ought to grow wider, since the sodium ions in the solution will oppose the entrance of the copper and cobalt ions into the permutite. In Experiment 4 a solution of the following composition: N/20 $CuCl_2$, N/20 $Co(NO_3)_2$, and N/1 NaCl, was passed through the sodium permutite. The column characteristics were:

$\underline{g}$ = 0.784 g, $\underline{L}_o$ = 3.9 cm, $\underline{A}$ = 0.385 sq cm, $\underline{W}$ = 0.522 g/ml, $S_{\underline{m}}$ = 2.30 mg eq/g, $\underline{Q}$ = 0.46 mg eq/cm.

The results are shown in Fig. 4. When the first milliliter of solution is poured in, two zones are formed, but the color intensity of each zone was much lower than in the preceding instances. At the end the cobalt zone was washed out and had no definite boundary. The color at the boundary between the two zones was an intermediate one. The cobalt began to get through as early as the addition of the third milliliter of solution, the emerging filtrate was pink. The color of the copper zone gradually and slowly increased throughout the duration of the test, but still remained paler than the color of the copper zone in the preceding tests. The copper is observed to get through after the tenth milliliter of solution is added; in the previous tests no copper was seen to get through – it was all retained in the column. The zone length increased linearly with the volume of solution:

$$\left.\begin{array}{l} \text{For the } Cu^{+2} \text{ zone} \;....\; \lambda_1 = 0.40\underline{v} + 0.3, \\ \text{For the } Co^{+2} \text{ zone} \;....\; \lambda_2 = 1.3\underline{v}. \end{array}\right\} \tag{8}$$

In this test the value of $\underline{c}^o/\underline{Q}$ was 0.11 per sq cm, i.e., the copper zone was about 3.5 times as long, and the cobalt zone about 12 times as long as the compact zone in the ideal chromatogram.

Thus, these tests demonstrate that the zone length rises linearly with the amount of cation added and that within the zones the previously adsorbed cation (in our instance, the sodium ion) is not completely forced out of the permutite. It should be noted that the appelation of the upper zone as the "copper zone" is somewhat conventional; the copper zone probably contains a slight trace of cobalt. The term for the lower zone is quite accurate, however: the cobalt zone contains no copper, as the emerging filtrate, which contains cobalt, contains no copper.

Lastly, Experiment 5 was devoted to study of the zone length when an extremely dilute solution, namely, a 1:1 mixture of N/100 $CuCl_2$ and N/100 $Co(NO_3)_2$, is filtered through the permutite. It is known [5] that when monovalent ions of the permutite are replaced by bivalent ions of the solution, the adsorption of the latter increases with the dilution of the solution. It was therefore to have been expected that in this experiment the zones should have been sharper and there would be little difference in length.

The characteristics of the column were as follows: $\underline{g}$ = 0.768 g, $\underline{L}_o$ = 4.0 cm, $\underline{d}$ = 0.7 cm, $\underline{A}$ = 0.385 sq cm, $\underline{W}$ = 0.50 g/ml, $\underline{S}_m$ = 2.30 mg eq/g, $\underline{Q}$ = 0.44 mg eq/cm.

When the first solution is poured into the column, a gray film first forms on the surface of the permutite, which then is differentiated into two thin rings -- sky-blue and pink -- which gradually grow wider. The boundary between the zones is sharply marked. The zone lengths were measured after each 10 ml of solution was poured through. A total of 50 ml of solution was used; both zones, copper and cobalt, were of identical length throughout the test.

$$\lambda = 0.02\underline{v} . \qquad (9)$$

The value of $\underline{c}^o/\underline{Q}$ is 0.01 per sq cm, i.e, the zones in the chromatogram are twice as long as in the compactly filled zones of the ideal chromatogram.

In Experiment 6 the length of the copper zone in cobalt permutite was studied.

Characteristics of the column: g = 0.519 g, $\underline{L}_o$ = 3.7 cm, $\underline{d}$ = 0.7 cm, $\underline{A}$ = 0.385 sq cm, $\underline{W}$ = 0.364 g/ml, $\underline{S}_m$ = 2.30 mg eq/g, $\underline{Q}$ = 0.32 mg eq/cm. Solution: N/20 $CuCl_2$.

The results are shown in Fig. 5. When the first milliliter of solution is poured into the column a grayish-blue zone 0.4 cm long is formed, followed by an intermediate zone of the same color with a lilac tint about 0.1 cm long, and at the bottom unchanged cobalt permutite. As more solution is poured in, the sky-blue zone grows wider, and the intermediate zone remains unchanged with the same length until the end of the test. The variation of zone length with volume of solution is given by the following equation:

$$\lambda_1 = 0.28\underline{v} + 0.15. \qquad (10)$$

The value of $\underline{c}^o/\underline{Q}$ is 0.16 per sq cm, i.e., in this case as well, the copper zone is about twice as long as in the ideal chromatogram.

Thus, the length of the cation zone as a function of the solution volume is given in the following equation for a constant cation concentration:

$$\lambda = \alpha\underline{v} + \beta. \qquad (11)$$

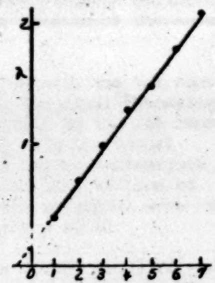

Fig. 5. Variation of the length of the Cu^{+2} zone in Co permutite with the volume of N/20 $CuCl_2$ solution.

The results are listed in the following table:

Test No.	$\underline{Q}$	α_1	α_2	β_1	β_2	$\underline{c}^0/\underline{Q}$
1	0.45	0.15	0.20	0.1	0.5	0.11
2	0.44	0.10	0.40	0	0.1	0.057 Cu^{+2} 0.170 Co^{+2}
3	0.33	0.18	–	0	–	0.15
4	0.46	0.40	1.3	0.3	0	0.11
5	0.44	0.02	0.02	0	0	0.01
6	0.32	0.28	–	0.15	–	0.16

Subscript $_1$ refers to copper; subscript $_2$ refers to cobalt.

In all tests with solutions of copper and cobalt salts (Nos. 1, 2, and 5), the length of the copper and cobalt zones is about twice as great as the length of the zone obtained with all the sodium ion driven out of the permutite. Introduction of a sodium salt into the solution widens the zone considerably (Experiment 4). The copper in the $CuCl_2$ solution forms a denser zone than the copper in the mixed Cu^{+2} and Co^{+2} solution (Experiment 1). In the cobalt permutite the length of the copper zone is twice what would correspond to complete expulsion of the cobalt ion from the permutite Experiment 6 . Hence, there is cobalt in the copper zone, probably within the permutite grains [8].

Moreover, it should be borne in mind that in reality in the pores of the adsorbent there is present a solution containing some quantity of each ion, so thatit is possible for λ and λ^0 to approach each other on the adsorbents large pore volumes.

The results obtained by us differ from those of Schwab and Dattler [2] cited above. In our experiments identical lengths of the copper-ion and cobalt-ion zones were observed only in Experiment 5, when extremely dilute solutions are filtered through the permutite. In the general case the lengths of the zones for the two ions is not found to be the same.

The variations of the zone length in the chromatogram with the ion concentration for constant solution volume is of interest. In the ideal chromatogram, the zone length for constant solution volume is proportional to the ion concentration, the coefficient of proportionality equaling $\underline{v}/\underline{Q}$. In the actual chromatogram the coincidence of the ratio of the initial ion concentrations with the ratio of the zone lengths is approximate in character. Let us look at Experiments 1 and 5, in which equimoler Cu^{+2} and Co^{+2} salt solutions were employed. The following were the zone lengths observed at $\underline{v}$ = 10 ml:

$$Cu^{+2}\text{:}\ \lambda_1' = 1.6\ \text{cm}\ (0.05\ N),\ \lambda_1'' = 0.2\ \text{cm}\ (0.005\ N),\ \lambda_1'/\lambda_1'' = 8,$$

$$Co^{+2}\text{:}\ \lambda_2' = 2.5\ \text{cm}\ (0.05\ N),\ \lambda_2'' = 0.2\ \text{cm}\ (0.005\ N),\ \lambda_2'/\lambda_2'' = 12.5.$$

Both ratios of zone length are close to 10, i.e. to the ratio of the initial concentrations.

The essential feature distinguishing the tests with permutite from those with basic aluminum oxide consists of the fact that during washing the zones do not grow as much wider as with aluminum oxide. This is due to the high absorptive power of permutite compared to that of alumina. Schwab and Dattler did not determine the absorptive capacity of basic aluminum oxide, and therefore their data cannot serve in determining the completeness of exchange in the zones as was done in our experiments.

But the length of zone for a given ion influences other cations as well. We saw that the presence of the same cations in the solution as in the permutite employed causes a considerable widening of the zones. Foreign cations, which are not colored, will act similarly.

The data cited indicate that the ratio between the zone length and the number of ions introduced into the column is semiquantitative. Precise quantitative analysis, based upon measuring the length of the zone of the given ion, is feasible only if the ion being measured is adsorbed many times more intensively than all the other ions present in the solution to be analyzed.

CONCLUSIONS

1. It has been established that there is a linear relationship:

$$\lambda = \alpha \underline{v} + \beta,$$

between the zone length of the cation in the exchange-ion chromatogram and the volume $\underline{v}$ of a solution of the same cation of definite concentration, where α and β are constants. The equation was derived from the Cu^{+2} Co^{+2} chromatogram.

2. Comparison of the coefficient α and the zone length in the ideal chromatogram makes it possible to demonstrate that both zones of the chromatogram contain the sodium ion together with one of the cations (Cu^{+2} and Co^{+2}).

3. The zone length is approximately proportional to the ion concentration in the initial solution for constant solution volume.

4. The length of the zones in the chromatogram depends on the concentration of the remaining ions in the solution; therefore chromatometry can be quantitative only for an ion whose adsorption is many times higher than that of the other ions.

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COMPUTING THE MOLECULAR VOLUMES OF INORGANIC COMPOUNDS OF THE $A_nB_mO_s$ TYPE

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After the discovery of X rays and the accumulation of sufficient numerical data from X-ray research on the magnitude of the distances between atoms and ions of various chemical elements, the effective radius of atoms and ions became the starting point for calculating molecular volume. In spite of this, V. Bilts [1] calculated molecular volumes independently of structural models, introducing the concept of increments for the individual elements.

The molecular volumes computed by Bilt's method mostly differ widely from the values for molecular volumes obtained experimentally. This is illustrated by the data of Table 1.

TABLE 1

No.	Compound	Molecular volume, determined experimentally	Molecular volume, computed by the Bilts method	Discrepancy
1	Li_3Hg	38.2	51.5	−13.3
2	NaHg	29.6	36.6	− 7.0
3	KHg_2	53.1	70.9	−17.8
4	$RbHg_6$	110.8	135.6	−24.8
5	$CsHg_{10}$	168.4	203.4	−35.0
6	NaSn	51.3	61.6	−10.3
7	Sr_3Ag_5	122.0	150.2	−28.2
	etc.			

It is therefore apparent that computing molecular volume by the Bilts method most often yields considerable deviations.

To compute the molecular volumes of compounds of the foregoing type $(A_{\underline{n}}B_{\underline{m}}O_{\underline{s}})$ we made use of the formula proposed by us to compute interatomic distances in compounds of this type.

In brief, this is the solution of the latter problem. In accordance with Coulomb's law, the mutual attraction between the B^{z+} and O ions should be:

$$\frac{z_2 z_3 e^2}{r^2}.$$

Now let us consider the instant when the anion $B_mO_s^{y-}$ and the cation A_n^{x+} approach each other to the distance of the radius required for their mutual attraction and the O_s^{f-} and A_n^{x+} ions mutually attract each other. As O_s^{f-} constitutes the intermediate bridge transmitting the mutual attraction of the O_s^{f-} and A_n^{x+} ions, on the one hand, and the attraction of the O_s^{f-} and B_m^{z+} ions on the other, the latter depends not only on the distance between them but also on the number of ions and molecules and on the magnitude of their charges. For instance, in $NaClO_4$, the Cl — O distance equals 1.59 Å; this distance is likewise 1.59 Å in $KClO_4$; in Ag_3PO_4 the P — O distance is 1.61 ± 0.03 Å; in BPO_4 this distance is 1.54 Å:, etc. Hence, the force of mutual attraction, F_1, between the ions of the anion $B_mO_s^{y-}$ when acted upon by the cation A_n^{x+}, from the empirical data cited above, must equal:

$$F_1 = \frac{Az_1z_2z_3z_4e^2}{r_1^2} \qquad (1)$$

Owing to the fact that their charges are of like sign, the A_n^{x+} and B_m^{z+} ions repel each other, the force of mutual repulsion, F_2, equaling:

$$F_2 = \frac{Az_1z_2e^2}{r_2^2}. \qquad (2)$$

From Equations (1) and (2) it is apparent that the repulsive forces will be positive, and the attractive forces negative, as the former will exist for like signs on z_1 and z_2 and the latter exists for unlike charges. Hence, summing up, we find that the aggregate attractive force F must be:

$$F = F_1 + F_2 = -\frac{Az_1z_2z_3z_4e^2}{r_1^2} + \frac{Az_1z_2e^2}{r_2^2}$$

where F = attractive force of the foregoing ions.

A = Madelung's constant, depending chiefly upon the number of ions in the molecule.

e = the charge on an electron.

z_1 = the amount of charge employed for the bond with element A.

z_2 = the amount of charge employed for the bond with element B

z_3 = the amount of charge employed for the bond with element O.

z_4 = the amount of charge employed for the bond between element O and one element of the cation.

r_1 = the distance between the B_m^{z+} and O_s^{f-} ions, i.e., $R_{z_2z_3}$.

r_2 = the cation radius, R_{z_1}

$$R_{z_1} + R_{z_2z_3} = R_{z_1z_2z_3} .$$

Since the anions ($B_mO_s^{y-}$) are present as individual structural units in the lattices of the salts of oxy-acids, the equilibrium distance between the elements making up the compounds must be calculated from the forces F_1 and F_2 separately, their sum constituting the aggregate attractive force F.

The energy of formation of the anion "U_1", arising as the result of the approaching of the ions (from infinity to the distance $R_{z_2z_3}$) will be:

$$\overset{\infty}{U}_1 = -\int^{R_{z_2z_3}} F_1 dr_1 = \int^{R_{z_2z_3}} \frac{z_1z_2z_3z_4e^2}{r_1^2} dr_1 = -\frac{z_1z_2z_3z_4e^2}{R_{z_2z_3}}$$

At the instant the ions with complete electron shells come into contact or approach each other, the force of repulsion, approximately equal to B/R^n, is generated; hence, the complete energy of interaction between the ions is:

$$U_1 = -\frac{Az_1z_2z_3z_4e^2}{R_{z_2z_3}} + \frac{B}{R^n_{z_2z_3}} . \qquad (4)$$

Upon differentiation of this equation we get:

$$\frac{dU_1}{dR} = \frac{Az_1z_2z_3z_4e^2}{R^2_{z_2z_3}} - \frac{nB}{R^{n+1}_{z_2z_3}}$$

The equilibrium distances are determined from the condition $\frac{dU_1}{dR} = 0$, i.e.,

$$\frac{nB}{R^{n+2}_{z_2z_3}} = \frac{Az_1z_2z_3z_4e^2}{R^2_{z_2z_3}}$$

whence:

$$nB = \frac{Az_1z_2z_3z_4e^2R^{n+1}_{z_2z_3}}{R^2_{z_2z_3}} = Az_1z_2z_3z_4e^2R^{n-1}_{z_2z_3} ;$$

whence,

$$R^{n-1}_{z_2z_3} = \frac{nB}{Az_1z_2z_3z_4e^2} .$$

and, moreover,

$$R_{z_2z_3} = \sqrt[n-1]{\frac{nB}{Az_1z_2z_3z_4e^2}} \qquad (5)$$

Assuming that we are dealing with univalent elements, we find from Equation (5) that:

$$R_{11}(z_2z_3) = \sqrt[n-1]{\frac{nB}{Ae^2}} \qquad (6)$$

For polyvalent ions, Equations (5) and (6) yield:

$$\frac{R_{z_2z_3}}{R_{11}(z_2z_3)} = \frac{1}{\sqrt[n-1]{z_1z_2z_3z_4}} ,$$

i.e.

$$R_{z_2z_3} = \frac{R_{11}\ z_2z_3}{\sqrt[n-1]{z_1z_2z_3z_4}} \qquad (7)$$

If we compute F_2 analogously from Equation (2), we get:

$$R_{z_1} = \frac{R_1(z_1)}{\sqrt[n-1]{z_1z_2}} \qquad (8)$$

As stated above, $R_{z_1} + R_{z_2z_3} = R_{z_1z_2z_3}$; hence, it follows from Equations (7) and (8) that:

$$R_{z_1z_2z_3} = \frac{R_{11}(z_2z_3)}{\sqrt[n-1]{z_1z_2z_3z_4}} + \frac{R_1(z_1)}{\sqrt[n-1]{z_1z_2}}$$

i.e.,

$$R_{z_1z_2z_3} = \frac{R_{11}(z_2z_3) + \sqrt[n-1]{z_3z_4}R_1(z_1)}{\sqrt[n-1]{z_1z_2z_3z_4}} \qquad (9)$$

We introduce the coefficient K of the coordination number to be expressed, and get:

$$R_{z_1z_2z_3} = K \cdot \left(\frac{R_{11}(z_2z_3) + {}^{n-1}\overline{z_3z_4}R_1(z_1)}{\sqrt[n-1]{z_1z_2z_3z_4}} \right) \qquad (10)$$

In this equation z_1, z_2, z_3, and z_4 denote valency charges that are already known. $R_{11}(z_2z_3)$ represents an expression for the sums of the radii of the "like-sign charge" ions of elements B and O, and the term $R_1(z_1)$ represents radius of the "like sign charge" ion A, which we have already defined; we have also defined n, the index of the degree of the coefficient of repulsion, and we therefore consider it advisable to insert at this point Table 2, in which there are listed the covalent radii for several elements.* This table also gives the values we assign to the coefficient of repulsion n; our definition of the coefficient of repulsion n is based upon the regularity of the ionization potential.

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* (together with the radii of the atoms of some metals.)

Table 2

		n	H 0.37									
	H 1.54	6	Li 0.78 1.34	Be 0.44 [illegible]	B 0.42 0.88	C 0.38 0.77	N 0.35 0.70	O 0.22 0.74	F 0.19 0.72			
O 1.76	F 1.33	7	Na 0.98 1.54	Mg 0.82 1.40	Al 0.72 1.26	Si 0.69 1.17	P 0.59 1.10	S 0.64 1.04	Cl 0.63 0.99			
S 2.20	Cl 1.81	8	K 1.33 1.96	Ca 1.17 -	Sc 1.03 -	Ti 0.88 1.36	V 0.82 -	Cr 0.81 -	Mn 0.75 -	Fe 0.92 1.26	Co 0.91 1.25	Ni 0.89 1.24
		8	Cu 0.96 1.35	Zn 0.83 1.31	Ga 0.81 1.37	Ge 0.76 1.22	As 0.71 1.21	Se 0.66 1.17	Br 0.62 1.14			
Se 2.29	Br 1.96	9	Rb 1.48 -	Sr 1.32 -	Y 1.20 -	Zr 1.07 -	Nb 0.98 1.37	Mo 0.90 -	Ma - -			
		7	Ag 1.13 1.53	Cd 1.06 1.48	In 1.02 1.44	Sn 0.96 1.40	Sb 0.89 1.41	Te 0.82 1.37	I 0.77 1.33			
Te 2.47	I 2.19	10	Cs 1.57 -	Ba 1.49 -	La 1.39 -	Hf - -	Ta - -	W 0.88 1.33	Re - -			
		12	Au - 1.50	Hg 1.25 1.48	Tl 1.15 1.47	Pb 1.06 1.46	Bi 0.98 1.45	Po - -	- -			

Note: To the right of the coefficient of repulsion "n" the first horizontal line (within each rectangle) shows the positive "like-sign charge" ionic radii for structures of coordination number 6 alongside the symbol for the respective element while the second line shows the covalent radii. At the left there are the negative "like-sign charge" ionic radii.

Since the first ionization potential gradually decreases in the elements of subbroup A (in the vertical columns of the periodic table as we go from the top to the bottom), the value we have assigned to the coefficient of repulsion n gradually rises correspondingly. As for the elements of subgroup B (in the vertical columns of rows I, II, III, and IV), the value of their first ionization potential diminishes only as far as the sixth horizontal row, then exhibiting a tendency to rise again. As a result, the value of the coefficient of repulsion n, assigned by us to the elements of sub group B, decreases down to the sixth horizontal row and then begins to rise again. On the basis of this behavior, we give a more precise value for n, the coefficient of repulsion. The values of the coordination number K were given by Zachariasen [2] in the form of a table; we used these values.

Assuming that the compounds are always in a state of greater or lesser ionization and rarely are purely ionic or purely homopolar compounds and that, therefore, most often we are dealing with an intermediate stage, we believe that the interatomic distance of a saturated ionic lattice should be computed like the radii of " like-sign charge" ions.

To compute the interatomic distance in a lattice in which the number of ionic bonds is smaller than the number of covalent bonds, it is advisable to use the method of mixed calculation, employing the covalent radii and the radii of " like-sign charge" ions, as the interatomic distance also depends on the type of bond involved.

As we are of the same opinion: that the effective radius of atoms or ions is the starting point for computing molecular volume, computing the magnitude of the molecular volume of compounds of the type mentioned requires the interatomic distance derived from Equation (10) proposed by us for determining the interatomic distance between the centers of the anion and cation, multiplied by the coefficient A and by 10^{-8} [for compounds of the $A_2(BO_4)_3$ type, coefficient A is 1.5 and equals unity for all the other compounds investigated by us]. The result is then cubed and multiplied by PN, i.e., by the number of atoms or ions (P) that make up the molecule, and by Avrogadro's number (N), after which it is divided by the sum of the ratio of the interatomic distance of the compound considered to the interatomic distance of the anion plus the coefficient of repulsion, n (= 9), multiplied by the constant $\underline{1}$ (= 0.1) .

Thus, the formula proposed by us for computing the molecular volume finally takes on the following form:

$$V = \frac{\left[\left(\dfrac{R_{11}(z_2z_3) + \sqrt[n-1]{z_3z_4}\cdot R_1(z_1)}{\sqrt[n-1]{z_1z_2z_3z_4}}\right) KA10^{-8}\right]^3 PN}{\underline{1}\cdot\left\{n + \left[\left(\dfrac{R_{11}(z_2z_3) + \sqrt[n-1]{z_3z_4}\cdot R_1(z_1)}{\sqrt[n-1]{z_1z_2z_3z_4}}\right) KA10^{-8} : \dfrac{R_{11}(z_2z_3)}{\sqrt[n-1]{z_1z_m}}\cdot 10^{-8}\right]\right\}},$$

where z_m = the aggregate sum of the charges employed for bonds with the ions (or atoms) that are interconnected with the central ion. Thus, for instance, in anions of the XO_3^{y} type, the aggregate sum of the charges employed by the O^{--}

ion for bonds to the central ion (or atom) as well as to the cation equals 6, while it equals 8 for anions of the XO_4^y type, 8 for anions of the $X_2O_4^y$ type, 14 for anions of the $X_2O_7^y$ type, and this sum is taken by us as equal to unity for $(CN)^-$ and $(NH_4)^+$, respectively.

Solving an example by means of the formula proposed by us for computing molecular volume is done as follows. Let us take as an example $NaIO_4$, for which n averages 7; $B_{11\,(z_2z_3)} = 0.77$ Å + 1.76 Å ; $R_{1\,(z_1)} = 0.98$ Å ; $z_1 = 1$; $z_2 = 7$; $z_3 = 2$; $z_4 = 1$; and $z_m = 8$; the coefficient K, expressing the co-ordination number, equals 1.044; the number of atoms entering into the composition of the molecule is 6; and coefficient A = 1. Hence,

$$V = \frac{\left[\left(\dfrac{0.77 + 1.76 + \sqrt[6]{2\cdot1\cdot0.98}}{\sqrt[6]{1\cdot7\cdot2\cdot1}}\right)\cdot1.044\cdot10^{-8}\right]^3\cdot6\cdot6.06\cdot10^{23}}{0.1\left\{9+\left[\left(\dfrac{0.77+1.76+\sqrt[6]{2\cdot1\cdot0.98}}{\sqrt[6]{1\cdot7\cdot2\cdot1}}\right)\cdot1.044\cdot10^{-8} : \dfrac{0.77+1.76}{\sqrt[6]{1\cdot8}}\cdot10^{-8}\right]\right\}} = 51.0 \text{ ml.}$$

The answer should have been 51.1 ml. Hence, the error is 0.1 ml, i.e., the agreement is extremely good. The precision of the formula proposed by us and of the method of computation was established by computing the molecular volumes for 170 compounds of the type mentioned above.

Some of them are listed in Tables 3, 4, and 5.

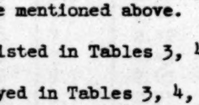
The notation employed in Tables 3, 4, and 5 is as follows: K = co-ordination number; n = coefficient of repulsion; R = interatomic distance between the cation and anion centers;

r = interatomic distance between the B and O ions (or atoms).

V = molecular volumes computed by our method.

$\frac{M}{d}$ = molecular volumes computed by dividing the molecular weight by the specific gravity.

In spite of the fact that — in the sense of our approach to the given problem — complex compounds have not been adequately investigated as yet and the need for their further study is evident, we still feel that consideration of the various complex compounds whose interatomic distances and molecular volumes were computed by our method is worth while. From these values it was possible to draw the following interesting conclusion. Let us take, for example, $K_3Fe(CN)_6$, the structure of which is represented, according to Ya. K. Syrkin and M.E.Dyatkina [3], by one of the following two variants



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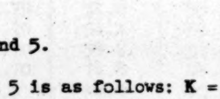

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TABLE 3

No.	Compound	K	n	R	r	V	$\frac{M}{d}$	discrepancy
1	$NaClO_3$	6	7	2.39	1.77	40.0	42.6	−2.6
2	$NaBrO_3$	6	7.3	2.42	1.77	41.5	45.2	−3.7
3	$AgBrO_3$	6	7.3	2.53	1.77	47.2	45.9	−1.9
4	$AgIO_3$	6	7	2.59	1.88	50.7	51.1	−0.4
5	$NaPO_3$	6	7	2.36	1.74	37.9	41.1	−3.2
6	KPO_3	6	7.3	2.67	1.74	54.6	52.3	−2.3
7	$CaSiO_3$	4	7.3	2.14	1.62	28.8	29.3	+0.5
8	Na_2SiO_3	4	7	2.37	1.82	47.0	50.9	−3.9
9	$MgTiO_3$	6	7.3	2.11	1.80	28.0	29.8	−1.8
10	$NiTiO_3$	6	7.7	2.23	1.80	32.8	30.5	+2.3
11	$FeTiO_3$	6	7.7	2.25	1.80	33.7	32.0	−1.7
12	$NaIO_4$	8	7	2.44	1.79	51.0	51.1	−0.1
13	$CoWO_4$	8	8.3	2.28	1.82	42.0	39.5	+2.5
14	$NiWO_4$	8	8.3	2.27	1.82	41.5	39.6	+1.9
15	$MgWO_4$	8	8	2.18	1.82	36.9	39.6	−2.7
16	$FeWO_4$	8	8.3	2.28	1.82	42.0	40.0	+2.0
17	$ZnWO_4$	8	8.3	2.22	1.82	38.9	40.2	−1.3
18	$CaMoO_4$	6	8	2.35	1.79	45.7	46.5	−0.8
19	$SrMoO_4$	6	8.3	2.50	1.79	54.6	52.0	+2.6
20	$PbMoO_4$	6	9.3	2.45	1.79	51.6	53.7	−2.1
21	Na_2SO_4	6	7	2.32	1.70	51.1	53.2	−2.1
22	Ag_2SO_4	6	7	2.43	1.70	58.4	57.0	+1.4
23	Tl_2SO_4	6	8.7	2.65	1.70	74.8	74.6	+0.2
24	$HgSO_4$	6	8.7	2.35	1.51	44.2	45.8	−1.6
25	$BaSO_4$	8	8	2.52	1.51	54.5	51.9	+2.6

In accordance with the two variants cited above, iron is linked to the cyanides (or to the cyanogen groups) by covalent bonds, whereas potassium has an ionic bond. Hence, the covalent radius should be taken for iron, and the radii of "single-charge" ions for the other components.

According to the structure shown in the first variant iron is octavalent and single-charged, i.e, a total of 9 electrons is involved in bonds; there remains one unpaired electron. In the second variant iron is heptavalent plus one unpaired electron, i.e., only 7 electrons are used for bonds. In the given compound the average value of n is 7, and the coefficient reflecting the coordination number equals unity, i.e., K = 1.

According to the structure indicated by the first variant the computation of the molecular volume of $K_3Fe(CN)_6$ is as follows:

$$V = \frac{\left[\left(\frac{1.26+1.92+\sqrt[6.5]{1\cdot 1\cdot 1.33}}{\sqrt[6]{1\cdot 9\cdot 1\cdot 1}}\right) 10^{-8}\right]^3 10\cdot 6.06\cdot 10^{23}}{0.1\left\{9+\left[\left(\frac{1.26+1.92+\sqrt[6.5]{1\cdot 1\cdot 1.33}}{\sqrt[6]{1\cdot 9\cdot 1\cdot 1}}\right)\cdot 10^{-8} : \frac{1.26+1.92}{\sqrt[6]{1\cdot 9}} 10^{-8}\right]\right\}} = 178.3 \text{ ml.}$$

It ought to be 177.9 ml, i.e., the error is merely 0.4 ml, which indicates good agreement of the results of computation with the experimental data.

TABLE 4

No.	Compound	K	n	R	r	V	$\frac{M}{d}$	Discrepancy
1	$NiAl_2O_4$ ...	6	7.3	2.17	1.56	41.7	39.4	+2.3
2	$CoAl_2O_4$ ...	6	7.3	2.19	1.56	42.8	39.7	+3.1
3	$CuAl_2O_4$ ...	6	7.3	2.23	1.56	45.1	39.7	+4.6
4	$MgAl_2O_4$ ...	6	7	2.07	1.56	36.4	39.7	−3.3
5	$ZnAl_2O_4$ ...	6	7.3	2.13	1.56	39.5	39.7	−0.2
6	$FeAl_2O_4$ ...	6	7.3	2.20	1.56	43.4	40.5	+2.9
7	$MnAl_2O_4$ ...	6	7.3	2.08	1.56	36.9	42.9	−6.0
8	$ZnCr_2O_4$ ...	6	7.7	2.23	1.68	35.5	33.3	+2.2
9	$NiCr_2O_4$ ...	6	7.7	2.27	1.68	47.9	43.3	+4.6
10	$MgCr_2O_4$ ...	6	7.3	2.17	1.68	42.1	43.4	−1.3
11	$CoCr_2O_4$ ...	6	7.7	2.29	1.68	49.1	43.6	+5.5
12	$FeCr_2O_4$ ...	6	7.7	2.30	1.68	49.8	44.0	+5.8
13	$MnCr_2O_4$ ...	6	7.7	2.17	1.68	42.1	45.5	−3.4
14	$CdCr_2O_4$ ...	6	7.3	2.35	1.68	52.9	48.2	+4.7
15	$MgIn_2O_4$ ...	6	7	2.25	1.75	47.0	51.8	−4.8
16	$CdIn_2O_4$ ...	6	7	2.43	1.75	58.6	56.0	+2.6
17	Ag_2CrO_4 ...	4	7.3	2.44	1.87	59.8	58.9	+0.9
18	$Ag_2Cr_2O_7$ ...	4	7.3	2.44	1.71	92.9	90.5	+2.4
19	Ag_2SeO_4 ...	6	7.3	2.48	1.76	62.1	60.1	+2.0
20	Tl_2SeO_4 ...	6	9	2.69	1.76	78.4	80.3	−1.9
21	$(NH_4)_2SeO_4$.	6	7	2.72	1.76	80.9	80.5	+0.4
22	Na_2SiF_6 ...	6	7	2.38	1.50	69.4	70.2	−0.8
23	$Ba(MnO_4)_2$..	6	8.3	2.53	1.64	102.4	99.5	−2.9
24	$Al_2(SO_4)_3$.	6	7	2.31	1.42	119.5	126.3	−6.8
25	Li_3PO_4	6	6.7	2.16	1.66	47.4	48.1	−0.7

The molecular volume of $K_3Fe(CN)_6$, on the basis of its structure corresponding to the second variant, is:

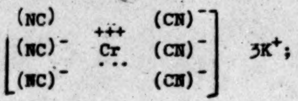
$$V = \frac{\left[\left(\frac{1.26+1.92+\sqrt[6.5]{1\cdot 1\cdot 1.33}}{\sqrt[6]{1\cdot 7\cdot 1\cdot 1}}\right)\cdot 10^{-8}\right]^{3} 10\cdot 6.06\cdot 10^{23}}{0.1\left\{9+\left[\frac{1.26+1.92+\sqrt[6.5]{1\cdot 1\cdot 1.33}}{\sqrt[6]{1\cdot 7\cdot 1\cdot 1}}\cdot 10^{-8} : \frac{1.26+1.92}{\sqrt[6]{1\cdot 7}}\cdot 10^{-8}\right]\right\}} = 198.7 \text{ ml.}$$

In practice, this volume cught to equal 177.9 ml, i.e., in this case the error involved is 20.8 ml. The agreement is good here as well, but the discrepancy is greater than in the first case. Hence, in the foregoing compound the structure is better expressed by the first variant.

Even more interesting are the results obtained for $K_3Cr(CN)_6$. Its structure may be expressed by any one of the following three variants:

TABLE 5

No.	Compound	K	n	R	r	V	$\frac{M}{d}$	discrepancy
1	$LiNO_3$	6	6	2.17	1.47	29.5	29.1	+0.4
2	$NaNO_3$	6	6.7	2.39	1.47	38.9	37.3	+1.2
3	$AgNO_3$	6	6.7	2.50	1.47	38.6	39.1	−0.5
4	$RbNO_3$	6	7.3	2.62	1.47	50.5	47.4	+3.1
5	NH_4NO_3	6	6.3	2.65	1.47	52.2	46.3	+5.9
6	$CsNO_3$	6	7.7	2.73	1.47	56.8	53.0	+3.8
7	$LiNbO_3$	6	7.3	2.08	2.12	27.3	31.6	−4.3
8	$CdTiO_3$	12	7.3	2.18	1.80	30.7	32.0	−1.3
9	$CaTiO_3$	12	7.7	2.32	1.80	36.8	33.2	+3.6
10	$NaNbO_3$	6	7.7	2.26	2.12	34.7	35.7	−1.0
11	$InBO_3$	6	6.7	2.29	1.29	33.7	30.8	+2.9
12	$LaBO_3$	9	7.7	2.33	1.29	37.5	37.6	−0.1
13	$MgCO_3$	6	6.7	2.14	1.36	28.1	27.4	+0.7
14	$ZnCO_3$,....	6	7	2.12	1.36	27.3	27.6	−0.3
15	$CoCO_3$	6	7	2.10	1.36	26.6	28.9	−2.3
16	$FeCO_3$	6	7	2.10	1.36	26.6	30.1	−3.5
17	$CdCO_3$	6	6.7	2.19	1.36	32.1	34.4	−2.3
18	$PbCO_3$	9	8.3	2.46	1.36	41.7	40.1	− 1.6
19	Li_2CO_3	4	6.3	2.16	1.54	35.2	35.0	+0.2
20	$ZrSiO_4$	8	7.7	2.24	1.65	39.4	40.2	−0.8
21	Mg_2SiO_4 ...	6	7	2.21	1.55	43.9	43.8	−0.1
22	$K_3CO(CN)_6$.	6	7	3.12	2.35	178.2	174.0	+4.2
23	$K_3Fe(CN)_6$.	6	7	3.12	2.36	178.3	177.9	+0.4
24	$K_3Cr(CN)_6$.	6	7	3.12	2.35	178.2	190.2	−12.0
25	BF_4K	4	7	2.43	1.81	50.4	50.4	−0.0



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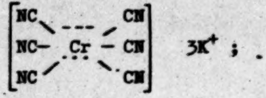

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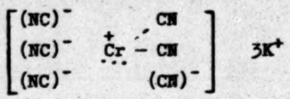

According to Ya K. Syrkin and M.E.Dyatkina [3], the existence of structures such as those expressed by the first and second variants is allowable under the concept of their being mutually superposed on one another; structures of other types, containing the same number of unpaired electrons, may likewise be imagined, such as the structure suggested by Ya. K. Syrkin and M.E.Dyatkina for the third variant. Computing the molecular volume for $K_3Cr(CN)_6$ for a structure as shown by the first variant, we find that it equals 219.2 ml, instead of the expected 190.2 ml, i.e., with a discrepancy of 29.0 ml; hence the structure assumed by the first variant is not very probable.

The molecular volume of $K_3Cr(CN)_6$, on the basis of the second variant's structure, as computed by our method is 178.2 ml instead of 190.2 ml; i.e., here, too, we have a discrepancy of 12.0 ml.

For the structure represented by the third variant the molecular volume of $K_3Cr(CN)_6$ as computed by our method is 217.0 ml. As the molecular volume is 190.2 ml for a structure assigned to the given compound by the third variant, the discrepancy resulting when the molecular volumes are compared totals 26.8 ml; i.e., in 11 cases we find good agreement between the experimental results and the computed figures. It must be assumed that the structure assigned to $K_3Fe(CN)_6$ by Ya. K. Syrkin and M.E. Dyatkina in the second variant predominates over all the other structures expressed by the other variants in the state of mutual superposition of one over another.

In conclusion it should be stated that the theoretical considerations we have set forth here make it possible to compute the molecular volumes of compounds of the foregoing type accurately by means of the formula proposed by us.

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THE ACTION OF PHOSPHORUS TRICHLORIDE OR PENTACHLORIDE UPON IODINE CHLORIDE AND IODINE BROMIDE, RESPECTIVELY

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In our paper on the PCl_5 – iodine system [1] we demonstrated that when these two substances react with each other, PCl_5 is first reduced to PCl_3 with the simultaneous oxidation of the iodine to iodine chloride ICl, which then combines with the as yet unreacted PCl_5 to form the complex compounds PCl_6I or $[PCl_4]\,[ICl_2]$.

These successive reactions may be expressed by the following equations:

$$PCl_5 + I_2 \rightleftarrows PCl_3 + 2ICl$$

$$\underline{2PCl_5 + 2ICl = 2PCl_6I}$$

$$3PCl_5 + I_2 = 2PCl_6I + PCl_3\ .$$

The results of some experiments, described in the preceding paper [1], gave us reason to believe that the first of these reactions is reversible.

We arrived at analogous conclusions with respect to the PBr_5 – iodine system, during the investigation of which we discovered the formation of the complex compound PBr_6I or $[PBr_4]\,[IBr_2]$, with PBr_3 and IBr as intermediate products [2].

These data made an investigation of the PCl_3 – ICl and PBr_3 – IBr systems seem promising.

There is no information in the literature on the behavior of PCl_3 toward ICl or of PBr_3 toward IBr, except for a statement in Walden's paper [3] that PCl_3 forms a dark-violet solution with ICl that is a nonconductor.

EXPERIMENTAL

The purification and quality of the preparations of PCl_3 and PBr_3 used by us have been described in our previous paper [1]. We prepared the ICl and IBr by the methods described in past papers issuing from our laboratory [4,5].

1. PCl_3 – ICl System

Thermal Analysis: When PCl_3 is added to iodine chloride, a lively reaction takes place, accompanied by the evolution of considerable heat. A dark-violet solution is formed, and on the walls of the vessel there appear crystals of the color of iodine and a crystalline substance that is dark orange in color.

The crystalline products formed in the PCl_3 – ICl system with PCl_3 content up to 10 mol. % were dissolved in the liquid mass upon shaking.

A eutectic was found at 10 mol. % of PCl_3 and 9.8°, (Table 1 and Fig. 1).

The fusibility curve rises very steeply after the eutectic point. Moreover, after 10 mol. % of PCl_3 a dark violet liquid is seen to form, its quantity increasing as more PCl_3 is added.

TABLE 1

Thermal Analysis System PCl_3–ICl

Mol. % PCl_3	Temperature arrest points	
	First	Second
ICl ...	27.2	
2.7 ...	24.5	
7.5 ...	18.0	
13.4 ...	36.8	9.8
13.9 ...	38.0	
14.8 ...	37.0	
30.3 ...	94.6	
36.0 ...	109.5	

More and more of a dark-brown, apparently inhomogeneous solid is precipitated out of the liquid. This fact, which testifies to profound chemical interaction occurring in the PCl_3 – ICl system, made it impossible to make a thermal analysis of this system at high PCl_3 concentrations. Tests were undertaken to establish the constitution of the liquid and solid phases.

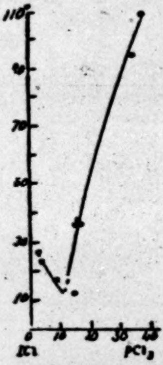

Fig.. 1.
Fusibility curve of the PCl_3--ICl system

The liquid was poured off and analyzed. Iodine and PCl_3 were detected in it. The solid mass was treated with CCl_4 (with heat) until new batches of CCl_4 used as a solvent remained colorless. As solution in CCl_4 progressed, the substance grew paler, and finally we obtained a yellowish-orange residue insoluble in CCl_4, which outwardly resembles the complex PCl_6I whose preparation and investigation were described in one of the previous papers, [1]. The substance obtained was heated to 80° to remove the traces of CCl_4 and was then analyzed for phosphorus and iodine content [1].

The results of analysis are listed in Table 2.

The results of the analysis give us grounds for holding that PCl_6I is formed (as in the PCl_5–I_2) during the reaction between PCl_3 and ICl.

Formation of the PCl_6I complex in the PCl_3 – ICl system may be due to the

TABLE 2

Results of Analysis of Substance Obtained in PCl_3 — ICl System

Alloy concentration mol.%	Weighed substance g	Iodine			Phosphorus		
		Expected computed per cent in terms of PCl_6I	Found		Expected computed per cent in terms of PCl_6I	Found	
			g	%		g	%
56.5	0.1705	34.24	0.0532	31.23	8.36	0.0143	8.29
68.9	0.9661	34.24	0.3296	34.19	8.36	0.0770	7.97

oxidation of the PCl_3 by the iodine chloride to form PCl_5 and the subsequent transformation of this PCl_3 — ICl system into the PCl_5 — ICl system.

The simplest kind of chemical reaction in the PCl_3 — ICl system would be the formation of a product in accordance with the following equation:

$$PCl_3 + ICl = PCl_4I$$

Experimental data, however, do not corroborate the formation of a complex of the composition PCl_4 in the system investigated by us.[*]

If the reaction between PCl_3 and ICl resulted in the formation of PCl_4I, we should, upon analysis of the solid phase, obtain the following values (in terms of PCl_4I): 42.28% for iodine and 10.32% for phosphorus. The values for phosphorus and iodine obtained by us are very close to the figures determining the composition of the compound PCl_6I.

Bearing in mind the results described above of the research into the PCl_3 — ICl system investigated by us, we may assert that the following chemical reactions may occur in this system.

$$PCl_3 + 2ICl \rightleftarrows PCl_5 + I_2 \cdots \qquad (1)$$

$$PCl_5 + ICl = Pcl_6I \qquad (2)$$

Both of these reactions may be summed up in the following equation:

$$PCl_3 + 3ICl = PCl_6I + I_2 \qquad (3)$$

The following supplementary experiments were made to demonstrate the reaction between PCl_3 and ICl actually follows the course indicated by the summary equation, forming PCl_6I.

Experiment 1. We took 4.42 g of ICl and 8.32 g of PCl_3 or 2.2 moles of PCl_3 per mole of ICl, i.e., a considerable excess of PCl_3 over the stoichiometrical relations between PCl_3 and ICl required by Equation (3). The weighed portions of these substances were placed in the vessel illustrated in Fig. 2. The reaction mass was heated to 80-85°, and the excess PCl_3 was driven off through the bent tube. A total of 6.44 g was driven off. The PCl_3 was colored a crimson-violet owing to the dissolution of iodine in it.

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[*] According to the literature data at our disposal there is no report of the existence of PCl_4I. The analogous compound, PBr_4I was prepared by Prinvault in 1872 [5]

After the PCl_3 had been driven off, there remained in the reaction vessel a solid, apparently heterogeneous, dark-brown substance, which we washed repeatedly with carbon tetrachloride as described above until we obtained a yellowish-orange residue, constituting iodine chlorophosphate, PCl_6I.

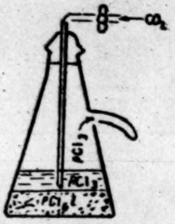

Fig.2. Reaction vessel

The results of analysis indicated that there were 2.06 g of iodine in the wash liquor (CCl_4), and 0.22 g of iodine in the PCl_3 driven off earlier; the total iodine found was 2.28 g, whereas 2.30 g of iodine should have been found, in terms of ICl, according to Equation (3).

Experiment 2. Weighed: 4.077 g of PCl_3 and 3.031 g of ICl, corresponding to 1.6 moles of PCl_3 per mole of ICl; this was heated in the vessel shown in Fig. 2 on an 80° water bath until all the excess PCl_3 had been eliminated. 3.536 g of liquid were driven off.

The dry solid mass left in the vessel was treated several times with carbon tetrachloride, as described above, until 1.751 g of a yellowish-orange substance — PCl_6I — was obtained.

In the driven-off liquid we found 0.329 g of iodine. From these figures it may be calculated that 0.870 g of the PCl_3 reacted with the quantity of ICl used. According to Equation (3) 0.854 g of PCl_3 should have entered into reaction with the ICl.

In the wash liquor, which constituted a solution of iodine and PCl_6I in CCl_4, we determined the amount of phosphorus.[*] 0.0367 g of phosphorus was found, corresponding to 0.4390 g of PCl_6I.

Thus, the total PCl_6I obtained under the conditions of this experiment was 2.190 g, which is very close to the theoretical quantity, 2.305 g, computed from Equation (3).

Electrical conductivity of the PCl_3 — ICl system was measured at the temperature of 45° and 55° in the concentration range from 4.2 to 19.5 mol.% PCl_3. When more PCl_3 was added, solid products made their appearance, which did not dissolve at the temperature of measurement (Table 1).

TABLE 3

Specific Electrical Conductivity of the PCl_3 — ICl System

Mol. % PCl_3	$\varkappa_{45}\cdot10^2$	$\varkappa_{55}\cdot10^2$
4.21	3.40	4.00
6.87	3.74	4.31
11.17	3.26	3.90
12.87	2.57	
19.50	1.72	

The results of measurement are listed in Table 3. The electrical conductivity of iodine chloride is $8.3\cdot10^{-3}$ mho at 45°.

The high electrical conductivity of the PCl_3 — ICl system, attained even at a low percentage of PCl_3, amounting to some 10^{-2} mho, is due to the formation of the PCl_6I complex, which is a strong electrolyte, within the system [1].

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[*] Phosphorus was determined by adding concentrated nitric acid to the given solution and boiling for 15-20 minutes. This oxidized the phosphorus to phosphoric acid, which was [illegible] determined by its precipitation as ammonium phosphomolybdate and subsequent dissolution in a N/10 alkali solution. The excess alkali was titrated with a N/10 acid solution.

As the PCl_3 percentage is raised, the electrical conductivity begins to drop. It is possible that this may be due to the fact that, according to Walden, who studied only solutions with low concentration of ICl and PCl_3, this system is a nonconductor.

2. PBr_3 – IBr System

Thermal analysis, performed for the interval from 0 to 87 mol.% of PBr_3, indicates the existence of a eutectic in this system at 33.6 mol.% of PBr_3 and 12.5° (Table 4 and Fig. 3).

TABLE 4

Thermal Analysis of the PBr_3 – IBr System

Mol.% PBr_3	Temperature arrest points in °C		
	First	Second	Third
—	40.0	–	–
1.16	38.6	–	–
11.25	28.5	–	–
13.20	25.6	–	–
23.50	18.2	–	–
33.60	–	15.5	–
35.03	21.6	17.5	–
40.20	21.7	13.5	–
41.90	22.5	13.5	–
46.30	17.5	15.0	–53
50.20	21.7	–	–58
61.10	21.5	–	–
74.90	34.1	–	–
87.20	39.5	–	–

Down to the proportions of the system's constituents represented by the eutectic the temperature arrest points are very sharp, being obtained with an undercooling that does not exceed 1-2°.

After the eutectic the solution is observed to stratify into two layers. The lower layer contains a substance that crystallizes in a temperature range from 13.5 to 22.5°. The upper layer, lighter in color, crystallizes at temperatures that are somewhat below the crystallization temperature of PBr_3, namely at –50°, –53°. As more PBr_3 is added, the size of the upper layer increases and the size of the lower layer correspondingly decreases. The temperatures beyond the eutectic are extremely inaccurate, being obtained with considerable undercooling.

At percentages of PBr_3 in excess of 50 mol.% crystallization most often takes place without noticeable temperature arrest points that are more or less prolonged. This may be due to the fact that the amount of the liquid phase increases, congealing at very low temperatures, and the quantity of the crystallizing lower layer diminishes, as a result of which it is quite possible that the thermal effect will be extremely small in this case.

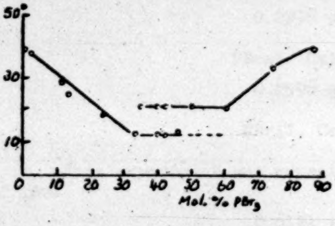

Fig. 3. Fusibility curve of the PBr_3--IBr system.

The causes set forth above probably account for the dispersion of the points along the temperature-concentration curve, and for the discrepancies in the temperature arrest points between repeated tests, which amount to as much as 4-5°.

All the results considered up to now enable us to isolate the following three lines of arrest points on the fusibility diagram of the PBr_3–IBr system beyond the eutectic ratio for PBr_3 and IBr:

a. At 21.5-22.5° (in the interval 35-61 mol.% of PBr_3).

b. At 12.5-13.5° (eutectic temperature).

c. At −53°.

Beginning with ~62 mol.% of PBr_3, the curve of first temperature arrest points begins to rise. Beyond 75 mol.% of PBr_3 measurement of the crystallization temperature yielded extremely inaccurate results.

These facts indicate the complex nature of the interaction between the components of the PBr_3 – IBr system.

We assumed that this interaction is of the same nature as in the analogous PCl_3 – ICl system, i.e., it consists in the formation of the PBr_6I, according to the following equation:

$$PBr_3 + 3IBr = PBr_6I + I_2. \tag{4}$$

In fact, if a small amount, say, of 1 mol.% of IBr is added to PBr_3, a residue is formed that outwardly resembles the PBr_6I complex that we obtained by the action of iodine upon PBr_5 [2]; in this process the liquid turns dark cherry-red, as is characteristic of a solution of iodine in PBr_3 [1].

Before commencing the isolation of PBr_6I from the products of the reaction between PBr_3 and IBr, we must choose a solvent in which iodine and IBr are easily soluble but which dissolves as little PBr_6I as possible. To do this we prepared PBr_6I by fusing together equimolar quantities of PBr_3 and IBr. The best solvents for the purpose set forth above turned out to be CS_2, PBr_3, and CCl_4. The composition of the residue formed in the PBr_3 – IBr system was determined as follows: a weighed amount of the fused substance, containing 51.1 mol.% of PBr_3 and 48.9 mol.% of IBr, was first treated with phosphorus tribromide until as much iodine had been leached out as possible, after which the residue was washed with carbon bisulfide (in which PBr_6I is slightly soluble), thus eliminating the remaining iodine, IBr, and PBr_3. The carbon bisulfide was eliminated by heating over a water bath at 50° or by means of a stream of dry CO_2 at room temperature. The substance thus obtained, comprising dark cherry-red needles, was analyzed as described in a previous paper [2].

0.2996 g substance: 4.68 ml 0.1 N $AgNO_3$.
Found %: I 19.83.
PBr_6I. Calculated %: I 19.91.

0.2996 g substance: 27.00 ml 0.1 N $AgNO_3$.
Found %: Br 72.69.
PBr_6I. Calculated %: Br 75.22.

This experiment was repeated, using 80.64 mol.% of PBr_3 and 19.36 mol.% of IBr.

0.6121 g substance: 9.5 ml 0.1 N $AgNO_3$.
Found %: I 19.53.
PBr_6I. Calculated %: I 19.91.

0.6121 g substance: 57.5 ml 0.1 N $AgNO_3$.
Found %: Br 75.07.
PBr_6I. Calculated %: Br 75.22.

It may be inferred from the results of the analysis that the complex compound PBr_6I is formed in the PBr_3 – IBr system as it is in the PBr_5 – iodine system.

Electrical conductivity of the PBr_3 – IBr system was measured at 45 and 55° (Table 5 and Fig. 4).

As was stated above, stratification is observed in the PBr_3 – IBr system beyond 33-34 mol.% PBr_3. The upper layer, which is lighter in color, is a nonconductor. The lower layer, a dark cherry-red and heavy, is a conductor. This layer was investigated at PBr_3 concentrations above 33 mol.%.

TABLE 5

Specific Electrical Conductivity of the PBr_3 – IBr System

Mol. % PBr_3	$x_{45^\circ}\cdot 10^2$	$x_{55^\circ}\cdot 10^2$	Temperature coefficient $C\cdot 10^2$
0	0.076		
9.9	2.61	2.83	0.77
13.2	3.12	3.33	0.65
16.5	2.22	2.53	
25.9	1.62	1.92	0.19
33.2	1.38	1.69	0.15
40.4	1.30	1.50	0.15
49.2	1.22	1.32	
59.1	1.22	1.48	0.25
64.4	1.20	1.51	0.25
71.8	1.20	1.50	0.25

When PBr_3 is added to IBr, the electrical conductivity first rises sharply, reaching its maximum value of ~ 0.03 mho at 13-15 mol.% of PBr_3, then slowly drops and finally remains constant (0.12 mho at 45° and 0.15 mho at 55°), the last measurements being made in the lower layer. This justifies the assumption that the composition of the lower layer is constant.

The high electrical conductivity of the PBr_3 – IBr system, which far exceeds the conductivity of phosphorus tribromide alone, testifies to the formation in this system of a new compound that is a strong electrolyte. According to our data, this electrolyte is $[PBr_3][IBr_2]$.

It is not without interest that minimum value of the temperature coefficient of conductivity occurs in a region of concentrations of PBr_3 that is close to the PBr_3-IBr ratio expressed by Equation (4).

3. Evaluation of Results

The research described above has proved that the complex compounds PCl_6I and PBr_6I are formed in the PCl_3-ICl and PBr_3 – IBr systems.

Formation of these complex compounds in these systems may be explained as follows: when PCl_3 or PBr_3 is reacted with ICl or IBr, respectively, the phosphorus trihalogenide is first oxidized to the pentahalogenide in accordance with this general equation (X = Cl or Br):

$$PX_3 + 2IX \rightleftarrows PX_5 + I_2.$$

The PX_5 formed unites with the as yet unreacted IX to form the complex $PX_5 \cdot IX$ or PX_6I:

$$PX_5 + IX = PX_6I.$$

Combining these two equations, we get:

$$PX_3 + 3IX = PX_6I + I_2.$$

The fact that the PX_6I complex represents a product of the union of the iodine in the halogenide IX with the phosphorus pentachloride PX_5, which in the the present instance is an intermediate product of the reaction between PX_3 and IX, may be proved as follows.

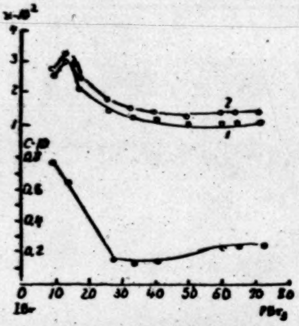

Fig. 4. Specific electrical conductivity of the PBr_3--IBr system.
1 - 45°
2 - 55°

Saturated solutions of PBr_5 and IBr in carbon bichloride were poured together. A precipitate was thrown down; this was filtered out by a glass filter fitted with a stopper containing a calcium-chloride tube (to prevent the action of atmospheric moisture) and then dried out at 50-55° in a stream of CO_2 until all the CS_2 has been eliminated. The same crystalline substance was obtained as when PBr_3 was reacted with IBr.

Analysis of this substance demonstrated that it is PBr_6I.

0.8312 g substance: 13.0 ml 0.1N $AgNO_3$.
Found %: I 19.82.
PBr_6I. Calculated %: I 19.91.

0.8312 g substance: 77.5 ml 0.1 N $AgNO_3$.
Found %: Br 74.51.
PBr_6I. Calculated %: Br 75.22.

0.8312 g substance: 60.1 ml 0.5 N NaOH.
Found %: P 4.83.
PBr_6I. Calculated %: P 4.86.

Comparison of the equation $PX_3 + 2IX \rightleftarrows PX_5 + I_2$ with the first of the equations expressing the reaction of PCl_5 or PBr_5 with iodine, namely, $PX_5 + I_2 \rightleftarrows PX_3 + 2IX$, confirms our assumption concerning the reversibility of these reactions.

Hence, it may be asserted that the $PCl_5 - I_2$ and $PCl_3 - ICl$ systems, as well as the $PBr_5 - I_2$ and $PBr_3 - IBr$ systems, are mutually interlinked.

CONCLUSIONS

1. The reaction of PCl_3 and ICl was investigated. It was established on the basis of exhaustive chemical analysis that the complex compound PCl_6I (or $PCl_5 \cdot ICl$) is formed in this system.

2. Analogously, the PBr_6I (or $PBr_5 \cdot IBr$) complex was prepared from the $PBr_3 - IBr$ system.

3. A mutual bond between the $PCl_5 - I_2$ and $PCl_3 - ICl$ systems, as well as between the $PBr_5 - I_2$ and $PBr_3 - IBr$ systems, has been proved.

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NEW CHEMICAL ELEMENTS -- THE BRILLIANT FORESIGHT OF D. I. MENDELEEV

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The history of the discovery and the present state of the periodic law have been the subject of a vast literature.

In the present paper I wish to deal solely with one problem that has not been fully illuminated as yet, in spite of its evident timeliness.

After the prediction and discovery of hafnium, the last "old" chemical element, four empty spaces were left in the periodic table: Nos. 43, 61, 85 and 87, and the efforts of chemists were directed to discovering the corresponding "new" chemical elements. But this could not be confined to the search for new chemical elements within the periodic table, even though the latter was the most obvious and essential task.

Long ago the irregularity of the periodic system was conspicuous — its breaking off fortuitously at the very beginning of the seventh period after the element uranium. It always seemed that there could and should be other chemical elements beyond uranium, the so-called transuranium elements, the discovery and study of which would be of no small theoretical and practical interest, if only because they all would obviously be radioactive. Thus, chemists' efforts were directed to the finding of new chemical elements to fill the spaces in the periodic table for the numbers 93, 94, 95, 96, etc.

No less obvious was the feasibility, aye, the necessity of developing the periodic table at the end that precedes its first period, its first element — hydrogen. As we know, D. I. Mendeleev was a supporter of this point of view. D.I. Mendeleev's scientific foresight with respect to the discovery of new chemical elements was both broad and deep.

Let us consider the prehydrogens. This term has not yet become current in scientific literature, although it is no less fitting, accurate, and necessary than the term "transuraniums". Its introduction points the way toward significant paths of progress, the undoubted development of the periodic system in another direction, beyond hydrogen.

The present-day notion of a chemical element must be expanded considerably by the introduction of at least some of the elementary particles, on terms of equality with them, out of which the atoms of chemical elements are built. In fact, the qualitative difference between the various chemical elements of increasing complexity from hydrogen to curium is based upon changes in the quantitative composition of the elementary particles that go to make them. The simplest element (up to the present time) — hydrogen — consists merely of a proton (plus neutrons in the case of its heavy isotopes) and an electron. But quantitative change may extend still further, and the different elementary particles (say, neutrons and electrons) may constitute even simpler chemical elements than hydrogen.

Modern theory foresees the possibility of forming atomic systems of a new type out of the elementary particles [1]. For instance, positronium is formed from an electron and a positron. The para-positronium atom, with dimensions of the order of the hydrogen atom, is found to be unstable, as the electron and the positron may be converted into two photons in a mean interval of time of the order of 10^{-10} sec. Ortho-positronium is transformed with the emission of three photons, and its life is about 100 times as long. Likewise, it is possible to have molecules of two atoms of positronium, as well as analogous systems consisting of a mesotron and an electron (mesotronium) or with two mesotrons (bimesotron). All of these systems will disintegrate after definite intervals of time. Their lives are at the limit of present-day methods of observation, and we must now expect the rapid discovery of similar metastable systems. Apparently, a whole new chapter in atomic chemistry will soon arise, devoted to these metastable ultralight isotopes, which will evidently be the first transhydrogens.

The first scientist bold enough to include the neutron in the periodic system and to identify it with the element "U" of D.I.Mendeleev (placed in the zero group ahead of hydrogen) was Prof. A.M. Vasilyev of the Kazan Institute of Chemical Technology [2].

This outstanding discovery has not been really evaluated up to the present time. This true evaluation, it seems to me, should be confirmed by giving a new name to the neutron as an element of the periodic system. I should suggest that it be named "mendelevium" in honor of D. I. Mendeleev. Some 12 years after A. M. Vasilyev's discovery there was published a paper dealing with the problem of including the elementary particles in the periodic system and assigning them definite places therein. This was the paper of E. I. Akhumov [3].

At present it is still hard to trace the outlines of the modern periodic system. It seems to me that the time for that has not yet come, as the theoretical and experimental data are not yet clearly evident. But its general contours are already visible, like the contours of the system as a whole in its dialectical development. This is no longer a lifeless scheme with a fixed beginning and end, with hardened and unchanging elements. This is a real reflection of eternally developing and transforming matter. This is the living history of the substance composing our planet. This is the real path, or at least its essential landmarks, marking the development of the nature we know.

And behind all the manifold varieties of our accumulated theoretical and experimental data, behind all the old, new, and newest chemical elements and their numberless chemical compounds, behind chemistry in its ordinary sense and behind the chemistry of nuclear transformations, and lastly, behind the contemporary chapter of atomic physics, dealing with the metastable ultralight isotopes, there stands the mighty figure of the venerable scientist D. I. Mendeleev, who eighty years ago wrote the "Essay on a system of the elements based upon their atomic weight and chemical resemblances."

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RESEARCHES IN THE FIELD OF QUINOLINE DERIVATIVES

V. JOINT CONDENSATION OF AROMATIC AMINES AND ETHYLENE GLYCOL WITH ACETONE AND METHYL ETHYL KETONE*

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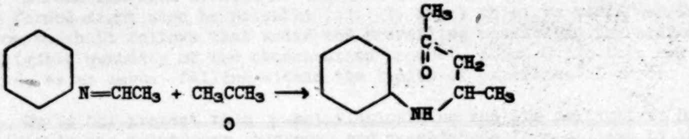
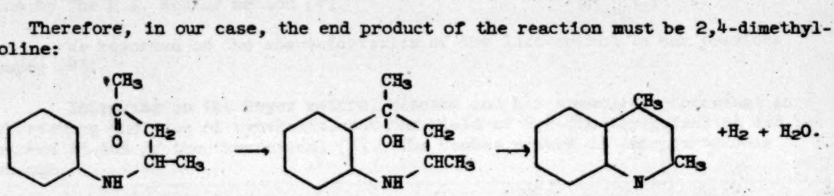
In our previous papers [1,2] we noted that in synthesizing quinoline derivatives from aromatic amines and ethylene glycol in a sulfuric-acid medium, among the principal intermediate reaction products are the monoethylideneaniline bases. These bases must react with the ketones [3], forming the corresponding derivatives of quinoline with substituents in the pyridine ring under specified conditions. Thus, the reaction of the aromatic amines with ethylene glycol [2], which is similar to the Skraup synthesis with glycerol, differs in principle from the latter in that it opens up the possibility of synthesizing the alkyl homologues of quinoline, containing substituents not only in the benzene ring but in the pyridine ring as well. For example, monoethylideneaniline, formed from aniline and ethylene glycol, must yield, when treated with acetone, a condensation product as shown in diagram (I).



(I)

which, according to Beyer [4], is also an intermediate product of the synthesis of 2,4-dimethylquinoline from aniline, acetone, and paraldehyde.

Therefore, in our case, the end product of the reaction must be 2,4-dimethylquinoline:



As hydrogen is evolved in the reaction, doubtless hydrogenating the 2,4-dimethylquinoline to the tetrahydro derivative [1], in turn the employment of an oxidant in this reaction is fully justified, as it is in the synthesis not using acetone, [1,2].*

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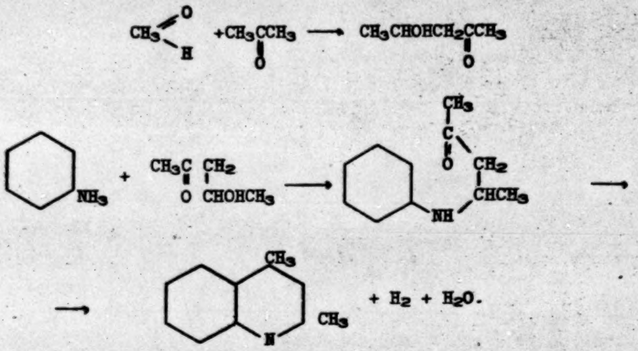
* The students G. N. Vytovskaya and N. I. Trubnikova participated in this research.

Beyer also admits the following reaction diagram (II) as one of the possibilities:



(II)

To resolve the question of the principal direction taken by the reaction we performed Experiment 10 in the absence of aniline and convinced ourselves that in our case no appreciable amount of the ketole is formed, which was to have been expected, as the acid medium does not facilitate an aldol condensation.

A reaction with aniline of the acetone itself or in the form of the mesityl oxide formed might also be possible [5]. To check this, we performed Experiment 9, from which it follows that under the prevailing conditions the acetone forms a negligible quantity of the condensation product, about 0.5%; this may really be ignored, as an amount falling within the limits of experimental error.

Up to the present time γ-methylquinaldine and its derivatives have been synthesized: the toluidines, acetone, and paraldehyde from aniline by the Beyer method in the presence of hydrochloric acid [4]; the toluidines and acetylacetone from aniline by the Combes method [6]; and the toluidines and acetylene from aniline by the N.S. Kozlov method [3].

We reported on the characteristics of the last method in our previous paper [2].

Improving on the Beyer method, Mikeska and his associates succeeded in shortening the time of synthesis, but the yield of 2,4-dimethylquinoline did not exceed 25-30% of the theoretical [7]. The Combes method is not practicable enough.

Besides these methods, 2,4-dimethylquinoline is formed with a good yield from acetanilide [8], which, in turn, is produced with a yield of 42% [9] from aniline and acetone or aniline and mesityl oxide [5]. The condensation of acetone with ortho aminoacetophenone likewise gives a very poor yield of 2,4-dimethylquinoline [10]. H.F.Tseou [11] and, more recently, R.H.F.Manske synthesized 2,4-dimethylquinoline from aniline and 4-ketopentane-2-ol, the latter with a yield of some 22% of the theoretical, in terms of aniline [12].

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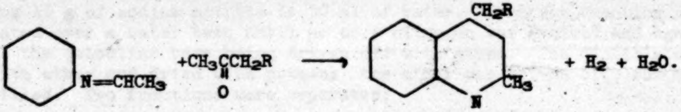
* There is no report of the successful employment of an oxidant in the Beyer reaction, effected in a hydrochloric-acid medium. (B.A.)

During our research we noted that the quinaldine formed in small amounts at the beginning of the reaction vanishes at the end of the reaction, as the methyl group apparently reacts with the acetaldehyde or acetone (Table).

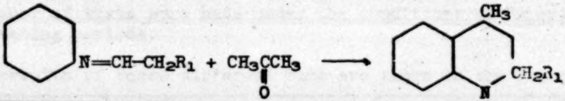
In a separate experiment, Experiment 11, quinaldine was reacted with ethylene glycol and acetone; it was found that about 10% of the quinaldine enters into the reaction under the conditions of the experiment. Apparently, the condensation products formed, which were mistaken by Beyer for biquinaldine in his method [4], partially accompany the 2,4-dimethylquinoline separated out. Driving off the water during the reaction, and increasing the yield of quinaldine in the synthesis from aniline and ethylene glycol [2], likewise result in an appreciable increase in yield.

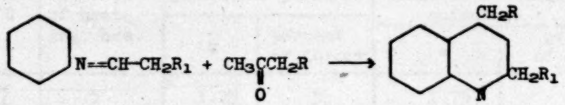
If methyl ethyl ketone is used instead of acetone, the principal reaction product is 2-methyl-4-ethylquinoline, though we might have expected 2,3,4-trimethylquinoline, owing to the mobility of the hydrogen atoms in the methylene group. The reaction follows the diagram:



Thus, in the present paper we propose a new method for the synthesis of alkylated quinaldines from cheap and easily available raw materials with satisfactory yields. It should be borne in mind that in this reaction ortho toluidine produces reduced yields, as in the synthesis without acetone [2].

When other alpha glycols are used with acetone, alpha-substituted lepidines may be formed [1], whereas when various methyl ketones are condensed with aromatic amines and alpha glycols, substituted quinolines should result:





The formation of tar during the reaction may be due to the polymerization of various unsaturated compounds, more of which are formed in this reaction than in the quinaldine synthesis from aromatic amines and ethylene glycol [2], at the expense of acetone condensation reactions.

EXPERIMENTAL

Raw materials: aniline, b.p. 183-184°; ethylene glycol, b.p. 196-197°;

acetone, b.p. 56-56.5°, bearing the label: "chemically pure, for analytical use". The use of a higher boiling acetone reduces the yield, and in the synthesis of crystalline 2,4,6-trimethylquinoline yields a partially tarry product that is hard to purify. Nitrobenzene, b.p. 209-211°; sulfuric acid, sp.gr. 1.84.

Synthesis of 2,4-Dimethylquinoline

Experiment 1: Into a 1-liter round-bottomed flask there was poured 15.5 g of aniline, 10 g of nitrobenzol, and 50 g of freshly prepared ethylene glycol. The ingredients were stirred together, and 34 ml of strong sulfuric acid was added. After careful stirring the flask was connected to a water reflux condenser through which 20 ml of acetone was passed drop by drop while the flask was gradually heated over an oil bath. Then the mixture was heated to the point of gentle boiling and kept there for 5 hours. Temperature of reaction: 140-145°. After the reaction was over, the mixture was cooled and diluted with water, after which the unreacted nitrobenzene was driven off with steam. The residue was alkalinized with a 40% solution of caustic soda, and the alkali was driven off with steam. The distillate was acidulated with 15 ml of strong sulfuric acid, cooled to room temperature by throwing pieces of ice into it, and diazotized to remove the aniline by adding 10 g of sodium nitrite in 50 ml of water. Then the reaction mixture was heated over a water bath until no more nitrogen was evolved and again alkalinized, the quinoline base being driven off with steam. The distillate was extracted with ether and dried with potash; the ether was driven off, and the base redistilled. Two fractions were separated:

1st fraction: 243-248°; n_D^{24} 1.58920; d_{24}^{24} 1.0392;

2nd fraction: 250-267°; n_D^{24} 1.59980; d_{24}^{24} 1.0506

The 243-248° fraction, 1.25 g of which was isolated, representing 5% of the theoretical yield based on aniline, is chiefly quinaldine; from it we prepared the picrate with a m.p. of 190° and the mercury salt with a m.p. of 165°.

The second fraction, 1.75 g of which was isolated, or 7% of the theoretical yield, is 2,4-dimethylquinoline. Its picrate had a m.p. of 192°.

A number of tests were made under the conditions of Experiment 1, using different heating periods.

The results of these different runs are shown in the following table.

Test No.	Temperature °C	Duration of heating, hrs.	Quinaldine yield		Yield of 2,4-dimethylquinoline		Boiling point °C
			g	percent of theory	g	percent of theory	
1	140° to 145°	5	1.25	5	1.75	7	250-267°
2		10	0.34	1.36	[illegible]	14.1	260-267
3		15	–	–	[illegible]	25.2	260-267
4		20	–	–	6.25	25.0	260-267
5		25	–	–	4.55	18.0	260-267

As is seen from the table, the quinaldine formed at first disappears after 15 hours of heating. The best yield of 2,4-dimethylquinoline is obtained by heating for 15-20 hours.

To determine the maximum yield of 2,4-dimethylquinoline, tests were made, involving driving off the water during the reaction; the results were good. One of these tests is cited here:

Experiment 6. Charge as in Experiment 1.

Heated for 10 hours to begin with, after which the water was driven off for 2 hours; some 20-25 ml was driven off, consisting of water together with the residual acetone and some of the nitrobenzene. Then 10 ml of acetone was added to the flask, and the mixture was heated for another 5-6 hours. Subsequent treatment as in Experiment 1. The yield of 2,4-dimethylquinoline with a b.p. of 260-267° was 7.55 g, or 30.2% of theoretical.

n_D^{22} 1.5995; d_{22}^{22} 1.0505.

Picrate b.p.: 192°.

Dumas' analysis for nitrogen:

0.1013 g substance: 8.0 ml N_2 (22°, 759 mm).

Found %: N 8.88.

$C_{11}H_{11}N$. Calculated %: N 8.90.

Synthesis of 2,4,6-Trimethylquinoline

Experiment 7. 17.9 g of p-toluidine, 11.5 g of p-nitrotoluene, 50 g of ethylene glycol, 5 g of sulfuric acid, sp.gr. 1.84, and 20 ml of acetone were charged into a 1-liter round-bottomed flask. The flask charging, the order of mixing of the reagents, and the heating were all as in the preceding experiment. After 10 hours of heating 25 ml of water was driven off within 2 hours, 10 ml of acetone was added, and the heating was continued for another 6 hours. The nitrobenzene and the separation of the toluidine were effected as in the previous experiment. After the 2,4,6-trimethylquinoline had been driven off by steam, it was filtered out and dried over caustic soda. The end product was white needles with a m.p. of 38°. The yield was 7.92 g, or 28% of the theoretical. The m.p. of the picrate was 202°. The double salt with mercuric chloride fused at 155°.

Dumas' analysis for nitrogen:

0.1000 g substance: 7.5 ml N_2 (24°, 743.2 mm).

Found %: N 8.17.

$C_{12}H_{13}N$. Calculated %: N 8.20.

Synthesis of 2,4,8-Trimethylquinoline

Experiment 8. This experiment was similar to the preceding one. Ortho toluidine and o-nitrotoluene were used instead of p-toluidine and p-nitrotoluene. The synthesized product was a thick oily liquid, dark brown in color and with a characteristic odor, b.p. 275-282°. The yield was 2.78 g, or 10% of the theoretical. The m.p. of the picrate was 190°, and of the mercury salt 233°; this corresponds to the literature data for 2,4,8-trimethylquinoline [3]. Part of the product crystallized upon standing.

Dumas' analysis for nitrogen:

0.1342 g substance: 9.9 ml N_2 (23°, 742.5 mm).
Found %: N 8.08.
$C_{12}H_{13}N$. Calculated %: N 8.20

Experiments 9 and 10 were performed to resolve the question of what was the principal reaction in the above procedure.

Experiment 9 was set up to check the possibility of the acetone itself reacting to form 2,4-dimethylquinoline under the given conditions. All the raw materials were taken in the same quantities and proportions as in Experiment 1, except for the ethylene glycol, which was not used in the reaction. Heating lasted 10 hours. Then 0.125 g of 2,4-dimethylquinoline was isolated by the usual method, representing 0.5% of the theoretical yield.

Experiment 10 was set up to convince ourselves of the formation of the ketole from the acetaldehyde and acetone under the given conditions, as assumed by Beyer. All the raw materials with the exception of aniline were used in the reaction. After heating for 10 hours, followed by cooling, the reaction mixture was alkalinized and then extracted with ether. After drying, the ether extract was distilled; the yield of reaction products with a b.p. of 70-125° was about 1 g.

Thus, the formation of a ketole in any appreciable quantities was not confirmed experimentally, and the direction of the reaction such as to form the ketole is evidently not the principal reaction.

Experiment 11 was performed to determine the possibility of changes occurring with the quinaldine or, analogously, with the 2,4-dimethylquinoline, as well as to compute these changes quantitatively.

Experiment 11. 10 g of quinaldine, 30 g of ethylene glycol, 15 g of acetone, and 30 ml of sulfuric acid, sp.gr. 1.84, were heated together in a round-bottomed flask with a water-cooled condenser over an oil bath for 20 hours at 140-145°. After acidulation of the reaction mass and steam distillation, the product was extracted with ether, and the ether extract was dried with potash and distilled. Two fractions were separated:

1st fraction: 243-247°: 6.5 g.

2nd fraction: above 255°: 1.0 g.

Thus the loss of quinaldine due to tarring was 2.5 g, whereas 6.5 g did not react, and 1.0 g, or about 10% of the quinaldine used, entered into the reaction with acetone and acetaldehyde to form the liquid condensation products.

The first fraction yielded a picrate with a m.p. of 190°, corresponding to quinaldine picrate. The second fraction is probably a mixture of quinaldine and the product of the reaction of quinaldine with acetaldehyde or acetone at the expense of the active hydrogen atoms of the methyl groups. It was not subjected to further study.

Synthesis of 2-Methyl-4-ethylquinoline

Experiment 12. The experiment was similar to Experiment 6, except for the substitution of methyl ethyl ketone for acetone. After the unreacted aniline had been eliminated by diazotization, the reaction mixture was alkalinized and steam-distilled, yielding slightly greasy crystals. These crystals were filtered out and pressed between sheets of filter paper. At the end of distillation a pure product distilled over, consisting of thin, colorless needles, which tended to cluster somewhat and were deposited on the walls of the flask. Yield: 4.6 g, or 16.2% of the theoretical. After crystallization from dilute alcohol the m.p. was 108°. The 2-methyl-4-ethylquinoline produced from the anilide of methyl ethyl ketone by Knowenagel's method was described by Bahr as an oily liquid, which in alcoholic solution forms a salt with tartaric acid having a m.p. of 155°. Bahr was unable to isolate the pure substance, apparently because of traces of 2,4-dimethylquinoline formed during the Knowenagel reaction [13]. The picrate precipitated from the alcoholic solution had a m.p. of 219°. 4-Ethylquinaldine is soluble at ordinary temperature in alcohol, ether, benzene, chloroform, and acetone.

Dumas' analysis for nitrogen:

0.1552 g substance: 11.4 ml N_2 (18.7°, 742 mm).
Found %: N 8.23.
$C_{12}H_{13}N$. Calculated %: N 8.20.

When a solution of platinum chloride in hydrochloric acid is added to a solution of the base in hydrochloric acid, a yellow precipitate of the double salt is thrown down at once. It crystallizes out of boiling dilute hydrochloric acid as tiny orange crystals. For analysis these crystals were washed successively with water, alcohol, and ether. They soften at 250° and finally melt at 278°. They lose two molecules of water when dried at 110°.

0.2200 g substance: 0.0098 g H_2O; 0.0540 g Pt.
Found %: Pt 24.55; H_2O 4.46.
$(C_{12}H_{13}N \cdot HCl)_2PtCl_4 + 2H_2O$. Calculated %: Pt 24.78; H_2O 4.57.

The bichromate of the base is precipitated from a sulfuric-acid solution as a dirty yellow precipitate when a solution of potassium bichromate is added. It is crystallized from hot water, in which it is soluble with difficulty, as beautiful yellow needles.

0.2430 g substance: 0.0667 g Cr_2O_3.
Found %: Cr_2O_3 27.45.
$(C_{12}H_{13}N)_2 \cdot H_2Cr_2O_7$. Calculated %: Cr_2O_3 27.14.

If the 4-ethylquinaldine is not filtered out of the distillate, but is extracted with ether, we are then able to drive off a tiny quantity, about 1 g, of a fraction that boils at 262-267°, from which it is easy to prepare the chloroplatinate of 2,3,4-trimethylquinoline, with a m.p. of 215°. Its picrate, precipitated from an alcoholic solution, has a m.p. of 192°.

CONCLUSIONS

1. The corresponding γ-methyl-substituted quinaldines have been prepared from aniline, p- and o-toluidines, acetone, and ethylene glycol in the presence of nitrobenzene or n- or p-nitrotoluene and of sulfuric acid.

2. Study of the mechanism of the reaction indicates that the principal direction of the reaction is the condensation with acetone of the monoethylidene-

aniline base initially formed, followed by the cyclization of the carbonyl bases formed into γ-derivatives of quinoline.

3. In the joint condensation of aniline, methyl ethyl ketone, and ethylene glycol in the presence of nitrobenzene and sulfuric acid the principal reaction product is 4-ethylquinaldine, which testifies that the hydrogen of the methyl group directly linked to the carbonyl group enters into condensation reaction with the methyl ethyl ketone.

4. It was noted that the 2-methyl-4-ethylquinoline inaccurately described by Bahr as an oily product actually is a crystalline substance with a m.p. of 108°.

5. The reaction of the aromatic amines with the methyl ketones and ethylene glycol is considered as a special case of a new, technically feasible method of synthesizing homologues of quinoline from the aromatic amines, ketones, and α-glycols, which is of practical and theoretical interest.

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THE ELECTROLYTICAL REDUCTION OF GLUCOSE

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At the end of the last century Fischer [1] and his associates developed a method for the production of sorbite and mannite by the reduction of glucose with sodium amalgam. Ipatieff's method [2] of producing these alcohols by the catalytic hydrogenation of the monoses by molecular hydrogen in an alkaline medium under pressure, up to 150 atm, and at high temperatures, up to 150°, is more economical. Even more efficient was the electrolytic method [3]. As we know the electrolytical reduction of glucose is less satisfactory [4] in an acid medium than in an alkaline electrolyte [5].

Our research was undertaken in order to shed light on the whole process of the electrolytical reduction of glucose in an alkaline medium.

Precise determination of the composition of the catholyte * indicated that the best conducting salt was sodium sulfate, followed by lithium sulfate. Other salts (magnesium sulfate, potassium aluminum sulfate, and potassium chrome alum) turned out to be less useful, owing to their low utilization of the current. All subsequent experiments were made exclusively with sodium sulfate.

As an alkali is formed at the cathode in the process of electrolysis, we studied the problem of the need for special additions of alkali to the initial catholyte. At a fixed glucose concentration

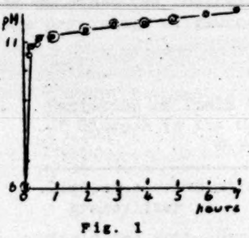

Fig. 1

O Expt. 77 C Expt. 79

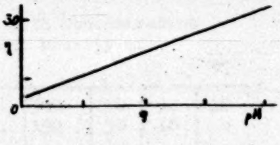

Fig. 2

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* In all our tests a N/1 solution of sulfuric acid served as the anolyte.

of 120 g/liter we varied the concentration of sodium sulfate from 75 g/liter (Experiment 79) to 150 g/liter (Experiment 77). Electrolysis was effected at a temperature of 20-24° and a current density of 1.5 amp/sq dm. As is seen in Fig. 1, the alkalinity rose rapidly in both cases, the pH value rising to 11.3 within an hour, and continuing to rise, though more slowly, thereafter. Thus, if we operate a catholyte with alkalinity of pH = 8-9, there is no need to add caustic soda to the electrolyte; on the contrary, arrangements must be made for acidulating the catholyte regularly. This regulation may be effected by changing the concentration of the sulfuric-acid solution in the anolyte and maintaining the difference in level between the anolyte and catholyte. Kirchhoff and Korzin give a wide pH interval (7-10) for producing pure sorbite. For the same purpose Creighton especially recommends a concentration of caustic soda as high as 20 g/liter and a pH = 8-9. With increased alkalinity a mixture of sorbite (about 80%) and mannite (about 20%) is obtained.

The variation of current utilization with pH of the electrolyte is shown in Table 1 and Fig. 2.

TABLE 1

Variation of Yield per Unit Current with Electrolyte pH at a Lead-Amalgam Cathode. Current Density 1.5 Amp/Sq. Dm. Glucose Concentration 120 g/liter. Temperature 20 - 24°.

pH of catholyte	10.85	9.1	8.7	8.2
Yield per unit current, %	32.1	20.3	-	11.9

Extrapolating these figures linearly, we may conclude that reduction of glucose practically ceases in an electrolyte with a pH = 6. This apparently explains the failure of a number of researchers to produce sorbite by the electrolytical reduction of glucose in an acid medium. According to Creighton's researches, increasing the concentration of mannose in the catholyte lowers the efficiency of current utilization.

In our glucose experiments we, on the other hand, found a definite improvement in yields per unit current when the glucose concentrations were increased, as was to have been expected. For example, using a cathode consisting of a nickel-aluminum alloy, a temperature of 20-25°, and a pH of the electrolyte of 10-11, we obtained the following picture of the variation of current utilization with the percentage of glucose in the electrolyte (Table 2).

TABLE 2

Variation of Yield Per Unit Current with Concentration of Glucose in the Catholyte at Current Density of 0.9 Amp/Sq.Dm.

Glucose concentration, grams/liter	initial....	300	150	50	10
	terminal ..	150	50	10	4
Yield per unit current in %		83	50	15	4

The velocity of reduction of the glucose as a function of the quantity of electricity passing through the cell also is convincing proof of the advantage of using high glucose concentrations (Fig. 3).

Furthermore, the rate of reduction of the depolarizer (glucose), according to the law of mass action, is proportional to the concentration of active hydrogen, while the latter concentration varies directly as the cathode potential. On the other hand, in the hydrogenation of organic compounds the catalytic action of certain metals is of exceptional importance; that is why special significance attaches to the choice of the cathode material in this case.

All researchers, with the exception of Creighton, electrolyzed glucose with a mercury cathode. Creighton tried out many metals and found that amalgamated lead was the best cathode material. When chemically pure lead and mercury were used, the electrolytic process was worse, whereas no reduction took place at all with iron and copper cathodes.

The tests made by us indicated that best results were obtained with a cathode made of a nickel-aluminum alloy and one made of amalgamated lead (Table 3).

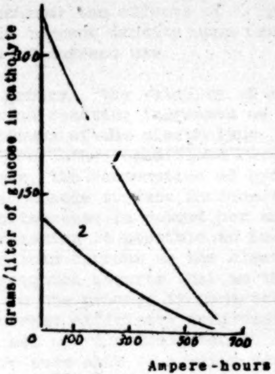

Fig.3

1-Initial concentration, 300 g glucose per liter; 2 - initial concentration, 120 g glucose per liter.

TABLE 3

Variation of Output per Unit Current With Cathode Material.
Temperature: 20-25°, Current Density: 0.9 Amp/Sq. Dm.
Glucose Concentration: 120 g/liter.

Cathode material	Al-Ni Alloy[*]	Pb	Cd	Zn	Ni	Al	Galvanized iron	Fe	Cu
Not amalgamated	53	–	19	15	6	5	0	0	0
Amalgamated	—	38	18	18	12	10	19	–	21

As is seen in Table 3, amalgamation levels out the properties of the cathode material.

Proper choice of the diaphragm and circulation of the electrolyte play an essential role in the electrolytic reduction of the glucose. Separation of the anode and cathode areas is necessary because of the oxidation of the glucose and sorbite at the anode, resulting in the production of a mixture of hexites and organic acids that are hard to separate. To prevent unproductive losses of glucose by diffusion from the catholyte to the anolyte, the diaphragm must be of the non-filtering "no-pass" type and must be acid-resistant (to the anolyte) and alkali-resistant (to the catholyte). Porcelain diaphragms manufactured by the State Ceramic Research Institute met the specifications.

The high viscosity of the electrolyte makes it necessary to provide for artificial circulation of the catholyte to keep it constantly renewed around the electrode. The effect of this stirring is clearly demonstrated by the following two tests (Table 4). We still have to show the basic factors affecting electrolytic reduction: the effects of temperature and current density upon the efficiency of current use.

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[*] Al-Ni alloy composition = 1:1 and 3:10. Identical results obtained with both alloys.

TABLE 4

Variation of Output per Unit Current with Stirring of the Catholyte. Glucose Concentration: 120 g/liter. Temperature: 44°. Current Density 1 Amp/Sq Dm.

Test No	Stirring	Output per unit current in %
6	no	42.7
11	yes	50.0

In general, the velocity of a hydrogenation reaction increases as the temperature of the electrolyte rises. Hence, other conditions remaining the same, the consumption of hydrogen at the cathode surface increases, causing an increase in output per unit current or making it possible to increase the load current on the electrolyzer. Creighton asserts that an improvement in the process is observed only up to a certain point (~30°), above which the current efficiency progressively drops. As is seen in Table 5, our experiments do not confirm Creighton's observations. On the contrary, at high temperatures we were able to acheive almost quantitative utilization of current.

It should be stated, however, that signs of tarring appear in the catholyte at temperatures above 30°, probably because of decomposition of the glucose in the alkaline solution and an aldehyde condensation. The tarring progresses with rising temperature, and especially with increasing alkalinity of the electrolyte. To obtain a product the electrolysis must be conducted at room temperature, or the electrolyte must be decolorized with activated charcoal after the reduction process is over. Thus, whenever the amount of tarry substances and a brownish tint are of no importance, operation at higher temperatures must be recommended.

TABLE 5

Variations of the Process of Electrolytical Reduction of Glucose with Cathode Current Density and Temperature. Glucose Concentration: 120 grams per liter.

Test No	Mean temperature °C	Current density amps/Sq Dm	Output per unit current
28	20	3	12.6
39	20	2	22.2
48	20	2	21.2
30	20.5	1.5	27.9
40	21	1.5	32.1
50	20	0.9	38.4
33	27.5	2.65	34.7
34	26	1.77	45.0
35	28	1.5	45.7
36	27	[illegible]	[illegible]
37	27	0.9	56.2
43	59.5	5	90.6
45	59.5	3	94.2
46	59.5	0.9	97.4

The effect of cathode density is seen in Table 5 as well. The process improves as the cathode current density is diminished. By extrapolating the data given it may be demonstrated that no reduction of glucose takes place at all at high current densities. The importance of current density depends on temperature. For example, at 20° electrolytical reduction apparently ceases at a current density of 4-5 amps/sq dm, [illegible] at [illegible] ceases at a density of 6-7 amps/sq dm. As the temperature is increased, this "critical" current density rises sharply.

The expenditure of electricity per kg of sorbite was as follows in our experiments (Table 6).

The energy yield was computed on the basis of the following cathode potential for the given current density: 1 amp/sq dm = 1.71 v (at 0.5 amp/sq dm = 1.68 v), measured by us at a temperature of 20°. On the basis of what has been stated above it may be asserted that all consumption indexes will drop sharply as the temperature is raised.

TABLE 6

Consumption of Electricity per Kg of Sorbite. Electrolysis at 20°. Current Density: 0.9 amp/sq dm. Catholyte pH: 10. Bath Voltage: 5.5 v.

Glucose concentration, grams/liter	Electricity consumption, kw-hr/kg	Energy yield, %
300-150	2	50
150- 50	3.2	33
50- 10	10.8	9
10- 4	35.8	3

CONCLUSIONS

Experimental study of the problem of electrolytically reducing glucose, supplemented by a review of the literature, has demonstrated that the optimum conditions for the process involve cathodes of a Ni + Al alloy or amalgamated zinc, with the anode and cathode regions separated by a compact "nonfiltering" diaphragm. Raising the temperature and the alkalinity, stirring the electrolyte, and lowering the current density assist the process.

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THE THERMAL POLYMERIZATION OF SIMPLE ESTERS OF THE ALLYL PHENOLS

I. POLYMERIZATION OF THE METHYL, ETHYL, AND ISOPROPYL ESTERS OF 2-ALLYLPHENOL

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Up to the present time there has been almost no research into the polymerization of the simple esters of the allylphenols; it therefore was of considerable interest to study the given compounds experimentally in this respect, bearing in mind, moreover, that the meagre published data on this subject are quite contradictory.

Some authors of such compounds with an allyl side chain consider that they are chemically inert as far as polymerization is concerned.

P. P. Shorygin [1], for instance, makes the tendency toward polymerization depend on the presence of conjugated double bonds, explaining the inability of eugenol to polymerize as due to the absence of such conjugated bonds in the compound. But, on the other hand, the Dutch researcher van Romburgh [2] was the first to observe the thermal polymerization of methylchavicol: $p\text{-}CH_3OC_6H_4 - CH_2 - CH = CH_2$, under 48 hours of heating to 250°; he even isolated solid polymers.

Recently, van der Zanden [3] studied the thermal polymerization of methyl- and ethylchavicols in greater detail, isolating their dimers and trimers and proving the synthetic structure of the latter.

V.V.Razumovsky [4], in his electronic theory, taking into account the degree of mobility of the double bond electrons in allylbenzene and propenylbenzene, concludes that ability to polymerize is more clearly marked in the [illegible] hydrocarbon than in the latter. The propenyl (and isopropenyl) derivatives of benzene have been investigated by a number of authors, including Behal and Tiffeneau [5] and, recently, M. Grumer [6].

Thus, despite their relative inertness in polymerization it must be admitted that the allyl-substituted derivatives of benzene may exhibit this property under certain conditions.

We were especially interested in the following factors in the foregoing investigations:

1. Such compounds, which do not possess strongly marked polymerization activity, ought to yield polymers of low molecular weight -- dimers and trimers,

which might serve as models of the polymerizing process.

2. Testing the polymerizing ability of a compound that combines an allyl group with alkoxyl groups that differ in size and number and are attached at various positions of the benzene ring.

3. If the polymerization breaks off at the stage where linear dimers are formed, as in methyl and ethylchavicols according to van der Zanden's data [3], testing them for specific viscosity by the Staudinger method.

4. We were interested in the applicability of refractometry to controlling the course of the process.

5. Since the presence of methylated allylphenols in some natural resins is known (gum elemi, etc.), we hoped to be able to obtain practical information concerning applications of our products.

Polymerization was effected in a Carius furnace, fitted with a thermoregulator, for 200 hours at a temperature of 250°. The tube was opened after every 50 hours of heating, and the refractive index, specific gravity, and specific viscosity of the reaction mixture were determined. To ensure uniform polymerization conditions the whole charge was sealed into a tube of Jena glass after careful preliminary purification. The Jena glass tube was dried, after careful cleaning, in a tubular furnace at 200°.

As may be seen from Curves 1, 2, and 3, the changes in d^{20}_{20}, n^{20}_{D}, and η_{20} are regular in all cases, almost straight-line, except for a certain discontinuity in the isopropyl ester at the very beginning of polymerization. It is possible that this discontinuity is explained by the tendency of the isopropyl esters of the phenols toward isomerization, as already pointed out by Claisen.

It might be supposed that opening the tube, which was necessary to measure changes in the foregoing constants, would affect the process of polymerization. To explore this effect we set up a control test with the ethyl ester of 2-allylphenol

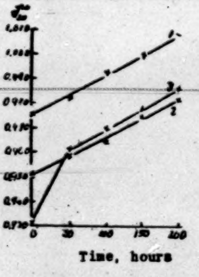


Fig.1 Change in specific gravity during polymerization of esters of 2-allylphenol: 1-methyl, 2-ethyl, and 3-isopropyl esters

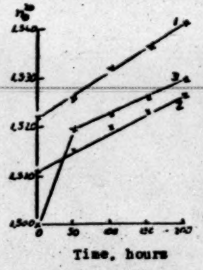


Fig.2 Change in refractive index during polymerization of esters of 2-allylphenol: 1-methyl, 2-ethyl, and 3-isopropyl esters.

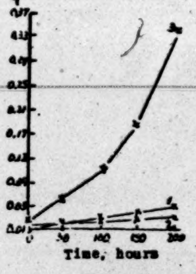


Fig.3 Change in relative viscosity during polymerization of esters of 2-allylphenol: 1-methyl, 2-ethyl, and 3-isopropyl esters.

as follows. Into each of four tubes identical in size and finish to the tube used in the first test, there was sealed 5 g of substance, and the tubes were heated under the same conditions. Then each tube was opened successively at stated intervals of time, and the same constants were measured. The data indicated that the discrepancies were insignificant, in every case being within the limits of experimental error. Thus, they varied from ± 0.0003 to ± 0.0020 for n_D^{20}; from ± 0.0006 to ± 0.0022 for d_{20}^{20}; and from ± 0.00031 to ± 0.00190 for η_{20}.

The reaction mixtures were subjected to vacuum distillation after completion of polymerization. First the unreacted monomers were driven off, and then at temperatures that were about 2 to 3 times as high, a viscous, slightly yellowed liquid. Some of the mixture – a tarry product that is insoluble in alkalis – remained undistilled in the flask. We did not fractionate the products in order to avoid high temperatures that approached the selected polymerization temperature, which might result in supplementary polymerization and spoil the picture of the dynamics obtained under our experimental conditions.

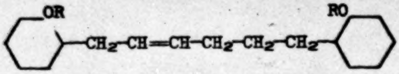
The second fractions (and the residues in the flasks) corresponded to the dimer forms, as the results achieved demonstrated. The molecular weight was determined in the usual manner by the Staudinger [ ] method specific viscosity η in a benzene solution. The values found: 0.0287 for the methyl ester; 0.0220 for the ethyl ester; and 0.0271 for the isopropyl ester, are very close to the η_{sp} of 1,6-diphenylhexane, determined by Staudinger and equaling 0.0255. If we bear in mind that side substituents have no noticeable effect on the specific viscosity when they are symmetrically arranged in the molecule, the basic skeleton of the dimer molecules should correspond to the skeleton of 1,6-diphenylhexane.

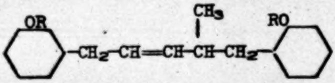
The fact that the refractive index increases as the process continues indicates that we are dealing with a condensation polymerization, in which the chain is quickly broken (chiefly in the dimerization stage); on the other hand, it turned out to be useful in checking the course of the process. With the distillation data and the values of d_{20}^{20} and n_D^{20} for the monomer and for the mixture after the process has been completed, it is possible to determine the specific refractive index and then the molecular refractive index for the dimers by the customary Lorentz-Lorentz formula. Considering that the second fractions and the flask residues correspond to the dimers, we obtained values that differ but little from those computed theoretically, as may be seen from the following tables.

Ester dimers	Mixture composition after polymerization		R of dimers	MR found	MR computed	Exaltation
	monomer	dimer				
Methyl....	46.45	53.55	0.3129	[illegible]	90.658	2.981
Ethyl.....	68.09	31.91	0.3081	[illegible]	99.893	0.069
Isopropyl.	34.85	65.15	0.3078	108.345	109.129	0.784

Research into the simple esters of the allylphenols indicated that they polymerize under the conditions selected by us: thus, 53.6% of the methyl ester polymerized, as did 21.91% of the ethyl ester and 65.15% of the isopropyl ester. In this process the polymerization of all the esters of the allylphenols stopped at the dimerization stage. This is shown by the molecular weight, the specific viscosity (Staudinger), the molecular refraction, and the presence of a single double bond in the dimer, determined by titration against a chloroform solution of bromine until slightly colored.

The presence of a double bond in the dimer molecule contradicts any cyclic formula for the dimer; it allows solely for a linear structure of the following two types:


(I)


(II)

for each of which it is theoretically possible to have several isomers, reflecting the position of the double bond, if secondary isomerization is present.

Assuming that a mixture of three isomers is formed in our case (we have not attempted their isolation as yet), we lean to Formula (I). This formula is confirmed by the specific viscosities. The unsymmetrical structure of Formula (II) excludes its coming under the Staudinger viscosity law. On the other hand, the stability of the dimers (the absence of further polymerization) likewise speaks in favor of the asymmetrical Formula (I) There ought to be a more clearly manifested tendency toward polymerization in the second type of molecule.

EXPERIMENTAL

Allyl phenolate was prepared by the method described by Hurd [8], with a yield of 74-75% of the theoretical in terms of phenol. The double-distilled product had the following constants:

B.p.: 88-90° (12 mm); 190° (698 mm); d^{20}_{20} 0.9815; n^{20}_{D} 1.5273; MR found: 41.94; MR computed: 41.33; exaltation: 0.61.

The data in the literature [9] for this ester are: b.p.: 192-195°; d^{15}_{15}, 0.9856; d^{25}_{25} 0.9777.

2-Allylphenol was prepared by rearranging the allyl phenolate as proposed by Claisen; to do this the ester was heated in a flask fitted with a reflux condenser over an oil bath at a temperature of 190-200° for [illegible] hours. Upon cooling the contents of the flask were dissolved in ether, and the 2-allylphenol was extracted with normal alkali. The alkaline solution was acidulated with hydrochloric acid, and the 2-allylphenol isolated was extracted with ether, dried with sodium sulfate, and vacuum distilled after the ether had been driven off. Yield: 72%.

B.p.: 101-103° (14 mm); 218-219° (702 mm); d^{20}_{20} 1.0161; n^{20}_{D} 1.5181; MR found: [illegible]; MR computed: 41.219; exaltation 0.329.

The data in the literature [10]: b.p. 109-110° (22 mm); 220° (760 mm); d^{15}_{15} 1.0255.

The methyl, ethyl, and isopropyl esters of 2-allylphenol were prepared by the method described [11], i.e., by heating 2-allylphenol with the corresponding halogen derivatives in an alcoholic solution of sodium ethylate.

The simple esters of 2-allylphenol were obtained with the following yields and constants:

Methyl ester: yield 62.8%;,

B.p. 60-62° (2 mm); d^{20}_{20} 0.9764; n^{20}_{D} 1.5232; *MR* found: 46.296; *MR* computed: 46.195; exaltation: 0.101.

Ethyl ester: yield 72.5%.

B.p. 70-71° (2 mm); d^{20}_{20} 0.9511; n^{20}_{D} 1.5110; *MR* found: 51.1[illegible]; *MR* computed:50.813; exaltation: 0.277.

3.64 mg substance: 10.95 mg CO_2; 2.83 mg H_2O.
Found %: C 82.09; H 8.68.
$C_{11}H_{14}O$. Calculated %: C 81.48; H 8.64.

Isopropyl ester: yield 48.3%

B.p.: 65° (2 mm); d^{20}_{20} 0.9315; n^{20}_{D} 1.5015; *MR* found: 55.661; *MR* computed: 55.813; exaltation 0.230.

4.12 mg substance: 12.36 mg CO_2; 3.34 mg H_2O.
Found %: C 80.58; H 9.0[illegible].
$C_{12}H_{16}O$. Calculated %: C 81.82; H 9.09.

The following constants are given in the literature [11] for the methyl ester of 2-allylphenol (o-allylanisole):

B.p. 86-87° (12 mm); 207° (761); d^{15}_{15} 0.9770; d^{24} 0.972; n^{22}_{D} 1.526.

The dimers of the methyl, ethyl, and isopropyl esters of 2-allylphenol were prepared by polymerizing them under the conditions described above and then isolating them by distillation in vacuum. They were all viscous liquids, slightly yellow in color, that were easily soluble in ether, benzene, chloroform, and acetone, and soluble with difficulty in alcohol.

Dimer of the methyl ester:

3.27 mg substance: 9.71 mg CO_2; 2.33 mg H_2O.
0.2132 g substance: 20.46 g benzene: Δt 0.180°.
Found %: C 81.03; H 7.97; *M* 290.
$C_{20}H_{24}O_2$. Calculated %: C 81.08; H 8.10; *M* 296.

Dimer of the ethyl ester:

3.81 mg substance: 11.89 mg CO_2; 3.10 mg H_2O.
0.1878 g substance: 21.15 g benzene: Δt 0.138°.
Found %: C 81.53; H 8.71; *M* 323.
$C_{22}H_{28}O_2$. Calculated %: C 81.48; H 8.64; *M* 324.

Dimer of the isopropyl ester:

2.67 mg substance: 8.02 mg CO_2; 2.07 mg H_2O.
[illegible] g substance: 18.93 g benzene: Δt 0.158°.
Found %: C 81.97; H 9.00; *M* 349.
$C_{24}H_{32}O_2$. Calculated %: C 81.82; H 9.09; *M* 352.

The alkoxy derivatives of the dimers were determined as follows:

$C_{18}H_{18}(OCH_3)_2$. Calculated 20.9; Found 19.79%;
$C_{18}H_{18}(OC_2H_5)_2$. " 27.7; " 28.16%;
$C_{18}H_{18}(OC_3H_7)_2$. " 33.4; " 31.52%.

In chloroform solution the dimers added bromine:

Dimer	Weighed portion g	Bromine added g	Computed stoichiometrically g
Methyl ester	0.2134	0.1198	0.1152
Ethyl ester...........	0.2958	0.1511	0.1460
Isopropyl ester......	0.2563	0.1203	0.1163

In all cases thick oily liquids were formed after the solvent had been removed. We did not succeed in isolating and identifying the dibromides in any instance, which seems to indicate the presence of a mixture of dimers.

CONCLUSIONS

1. The thermal polymerization of the methyl, ethyl, and isopropyl esters of 2-allylphenol in a homogeneous medium at a temperature of 250° was investigated.

2. It was found that the simple esters of 2-allylphenol polymerize under the given conditions only as far as the dimers.

3. The applicability of Staudinger's viscosimetric method to these dimers indicates their linear structure; this is also supported by the presence of double bonds in these dimers.

4. Refractometric measurements are applicable to the study of the polymerization of esters of 2-allylphenol.

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REACTIONS OF METALLO-ORGANIC COMPOUNDS WITH PHENOLS

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One of the present authors previously investigated the reactions of mercury compounds with the phenols, demonstrating [1] that new unsymmetrical derivatives of mercury are formed, in accordance with the equation:

$$(C_6H_5)_2Hg + RC_6H_4OH \longrightarrow C_6H_6 + C_6H_5HgC_6H_3(OH)R.$$

It appeared to be of interest to study the reactions of other metallo-organic compounds with the phenols [2], since there are no descriptions of such reactions in the literature. With this in view we studied the reactions of tetraphenyllead, tetraphenyltin, and triphenylbismuth with the following phenols: p-cresol, p-nitrophenol, and 2,4,6-trichlorophenol. It was established that the organic compounds of tin, lead, and bismuth react differently with the phenols than do the organic compounds of mercury.

Triphenylbismuth reacts most easily with the phenols. Even at 75-100° all the phenyl groups are cleaved within an hour, forming benzene and bismuth phenolates of various degrees of stability, according to the equation:

$$(C_6H_5)_3Bi + 3RC_6H_4OH \longrightarrow 3C_6H_6 + (RC_6H_4O)_3Bi.$$

Tetraphenyltin and tetraphenyllead enter into reaction with phenols only at 150°.

Tetraphenyltin reacts with the phenols to split off all the phenyl groups as benzene and to form blue resinous products that contain tin phenolates, which quickly lose their color when dissolved in alcohol or ether, separating out insoluble deposits with the following composition: $SnO_2 \cdot RC_6H_4OH$.

$$(C_6H_5)_4Sn + 4RC_6H_4OH \longrightarrow 4C_6H_6 + \underset{\displaystyle \downarrow \atop \displaystyle SnO_2 \cdot RC_6H_4OH}{(RC_6H_4O)_4Sn}$$

Tetraphenyllead splits off all the phenyl groups, forming benzene, when reacted with the phenols. The lead is thereby reduced, forming phenolates of bivalent lead, as in the equation:

$$(C_6H_5)_4Pb + 4RC_6H_4OH \longrightarrow 4C_6H_6 + (RC_6H_4O)_2Pb \text{ + oxidation products of the phenols.}$$

It should be pointed out that at 150° tetraphenyltin and tetraphenyllead are cleaved by 2,4,6-trichlorophenol, forming tin tetrachloride and lead chloride.

Our results justify making analogous assumptions (except for lead compounds) concerning the reactions of metallo-organic compounds with organic acids and phenols. While aromatic compounds of tin and bismuth completely split off all the aromatic radicals when they are reacted with organic acids, forming benzene and the corresponding salts [3], the aromatic compounds of mercury and lead substitute the acid radicals for half of their aromatic radicals, thus forming new stable derivatives [3].

EXPERIMENTAL

All experiments were performed by heating a mixture of the substances in sealed ampoules, using thermostats to regulate the temperature precisely.

1. Triphenylbismuth and p-Nitrophenol

The tests were run at 75-100° and lasted 1 to 3 hours. 0.3 g of p-nitrophenol was used for 0.3 g of triphenylbismuth. After heating the reaction mixture was orange in color. The formation of benzene was observed. After treatment with organic solvents (alcohol, ether, benzene) to leach out organic substances that contained no bismuth, there remained 0.13-0.18 g of an orange residue, a heavy crystalline powder that was insoluble and did not fuse up to 280°.

The experiment results are listed in the Table below.

Test No.	Temperature, °C	Time, hrs.	Amount of substance obtained, g	Analysis of Reaction Products			
				Weighed portion g	$BiPO_4$ produced, g	Bi found, g	Bi computed, %, for compounds
1	75	1	0.18	0.1016	0.0852	57.65	57.57 $BiO(OC_6H_4NO_2)$
2	75	3	0.15	0.1068	0.1010	65.09	65.48 $C_6H_4(OH)NO_2\cdot Bi_2O_3\cdot H_2O$
3	100	1	0.16	0.0966	0.0918	65.33	
4	100	3	0.13	0.0540	0.0552	70.28	69.20 $C_6H_4(OH)NO_2\cdot Bi_2O_3$

It follows from the tabular data, therefore, that $(O_2NC_6H_4O)BiO$ and $C6H_4(OH)NO_2\cdot Bi_2O_3$ are formed instead of $(O_2NC_6H_4O)_3Bi$, depending on the reaction conditions.

To establish the structure of the bismuth derivatives prepared they were treated in the cold with alcoholic HCl; this decolorized the substances at once and converted them quantitatively into p-nitrophenol with a m.p. of 112-114° (mixed sample 114°) and bismuth chloride.

2. Triphenylbismuth and p-Cresol

The tests were run at 100° and lasted 3 hours. 0.2 g of p-cresol was used for 0.2 g of triphenylbismuth. Benzene was observed to form. The reaction mass was light yellow in color. After treatment with solvents the residue was 0.08 g of an insoluble, infusible, light-yellow substance.

0.0550 g substance: 0.0561 g $BiPO_4$.
Found %: Bi 70.12.
$C_6H_4(OH)CH_3 \cdot Bi_2O_3 \cdot H_2O$. Calculated %: Bi 70.60.

3. Triphenylbismuth and 2,4,6-Trichlorophenol

The tests were run at 150° and lasted 3 hours. 0.3 g of trichlorophenol was used for 0.3 g of triphenylbismuth. The reaction mass was yellow in color. Benzene was observed to form. After treatment with organic solvents the residue consisted of 0.22 g of an insoluble and infusible substance, light yellow in color.

0.0988 g substance: 0.0384 g $BiPO_4$.
Found %: Bi 26.72.
$(Cl_3C_6H_2O)_3Bi$. Calculated %: Bi 26.17.

To establish the structure of the bismuth phenolate produced, the latter was treated with alcoholic HCl; this resulted in instantaneous dissolution, with the formation of trichlorophenol, m.p. 66-67° (mixed sample 67°), and bismuth chloride.

Thus, of the three phenolates of bismuth, the most stable proved to be the phenolate prepared from triphenylbismuth and trichlorophenol.

4. Tetraphenyltin and p-Nitrophenol

The tests were run at 150° and lasted 6 hours. 0.4 g of p-nitrophenol was used for 0.4 g of tetraphenyltin. The formation of benzene was observed. The reaction mass was a thick blue tarry mass, that was soluble in alcohol, benzene and ether. Upon standing, 0.06 g of an insoluble and infusible deposit settled out of the solution.

0.0550 g substance: 0.0258 g SnO_2.
Found %: Sn 36.96.
$C_6H_4(OH)NO_2 \cdot SnO_2 \cdot 2H_2O$. Calculated %: Sn 36.73.

5. Tetraphenyltin and p-Cresol

The tests were run at 150° and lasted 6 hours. 0.2 g of p-cresol was used for 0.4 g of tetraphenyltin. The reaction mass was a purple, thick liquid, soluble in alcohol, ether, and benzene, from which there settled out upon standing 0.08 g of an insoluble and infusible light yellow deposit.

0.0774 g substance: 0.0368 g SnO_2.
Found %: Sn 37.46.
$CH_3C_6H_4(OH) \cdot SnO_2 \cdot 3H_2O$. Calculated %: Sn 37.77.

6. Tetraphenyltin and 2,4,6-Trichlorophenol

The tests were run at 150° and lasted 3 to 9 hours. 0.2 g of trichlorophenol was used for 0.2 g of tetraphenyltin. The formation of benzene was observed. The reaction mass was dark in color. After treatment with organic solvents (leaching out the organic substances that contained no tin), the residue consisted of 0.055 g (theoretical value 0.07 g) of SnO_2, formed by the hydrolysis of $SnCl_4$.

7. Tetraphenyllead and p-Nitrophenol

The tests were run at 150° and lasted 3 to 9 hours. 0.3 g of p-nitrophenol was used for 0.3 g of tetraphenyllead. The reaction mass was orange in color. The formation of benzene was observed. After treatment with organic solvents there remained a residue weighing 0.22-0.25 g and consisting of a bright yellow, heavy, crystalline powder, insoluble and infusible up to 280°.

0.1200 g substance: 0.0653 g $PbSO_4$.
0.1500 g substance: 0.0824 g $PbSO_4$.
Found %: Pb 37.17, 37.51.
$2Pb(OC_6H_4NO_2)_2 \cdot C_6H_4(OH)NO_2$. Calculated %: Pb 37.46.

To establish the structure of the substance it was treated with alcoholic HCl; this caused the instantaneous decolorization of the substance in the cold, with the quantitative formation of lead chloride and p-nitrophenol, m.p. 112-114° (mixed sample 114°).

8. Tetraphenyllead and p-Cresol

The tests were run at 150° and lasted 3 to 6 hours. 0.2 g of p-cresol was used for 0.3 g of tetraphenyllead. After treatment of the reaction mass with organic solvents the residue consisted of 0.1 g of a light yellow substance, insoluble and infusible.

0.0850 g substance: 0.0567 g $PbSO_4$.
Found %: Pb 45.56.
$(CH_3C_6H_4O)_2Pb \cdot 2H_2O$. Calculated %: Pb 45.30.

9. Tetraphenyllead and 2,4,6-Trichlorophenol

The tests were run at 150° and lasted 3 to 6 hours. 0.2 g of trichlorophenol was used for 0.2 g of tetraphenyllead. The formation of benzene was observed. After treatment with organic solvents the residue was 0.08 g (theoretical value 0.11 g) of lead chloride.

Tetraphenyllead also reacts with ether phenols as has been described above for p-nitrophenol and p-cresol. According to A.M.Kartayeva, phenolates of bivalent lead are obtained as insoluble, infusible, often colored, powders with the following phenols: phenol, resorcinol, phloroglucinol, pyrogallol, o-nitrophenol, m-nitrophenol, trinitrophenol, p-bromophenol, tribromophenol, α-naphthol, and β-naphthol.

SUMMARY

1. Tetraphenyltin, tetraphenyllead, and triphenylbismuth, when reacted with phenols: p-cresol, p-nitrophenol, and 2,4,6-Trichlorophenol, completely split off the phenyl groups, forming benzene and phenolates of the respective metals of varying degrees of stability.

2. It was shown that in the reactions of the aromatic compounds of mercury, lead, tin and bismuth with the phenols and with the organic acids the process is almost completely analogous (with the exception of lead compounds).

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PREPARATION OF ETHYL γ-BROMOPROPYLMALONATE

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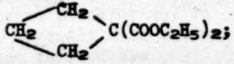
Wilstatter [1] produced ethyl γ-bromopropylmalonate by the action of sodium malonic ester upon trimethylene bromide, the yield being no more than 24-28% of theory. The reason for this low yield is that the γ-bromopropylmalonate initially formed undergoes further transformation during the reaction, as a result of which a rather complex mixture of products is finally obtained.

Theoretically, the following reactions are possible when sodium malonic ester acts upon trimethylene bromide:

$$\text{I. } Br - CH_2 - CH_2 - CH_2 - Br + NaCH(COOC_2H_5)_2 \longrightarrow NaBr + Br - CH_2 - \\ - CH_2 - CH_2 - CH(COOC_2H_5)_2;$$

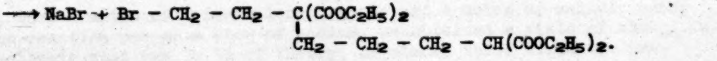
$$\text{II. } (C_2H_5OCO)_2CHNa + BrCH_2 - CH_2 - CH_2 - CH(COOC_2H_5)_2 \longrightarrow NaBr + \\ + (C_2H_5OCO)_2CH - CH_2 - CH_2 - CH_2 - CH(COOC_2H_5)_2;$$

$$\text{III. } BrCH_2 - CH_2 - CH_2 - CH(COOC_2H_5)_2 + NaCH(COOC_2H_5)_2 \rightleftharpoons BrCH_2 - \\ - CH_2 - CH_2 - CNa(COOC_2H_5)_2 + CH_2(COOC_2H_5)_2;$$

IV. $BrCH_2 - CH_2 - CH_2 - CNa(COOC_2H_5)_2 \longrightarrow NaBr +$ ;

$$\text{V. } BrCH_2 - CH_2 - CH_2 - CNa(COOC_2H_5)_2 + BrCH_2 - CH_2 - CH_2Br \longrightarrow NaBr + \\ + (BrCH_2 - CH_2 - CH_2)_2C(COOC_2H_5)_2.$$

$$\text{VI. } BrCH_2 - CH_2 - CH_2 - CNa(COOC_2H_5)_2 + \\ + BrCH_2 - CH_2 - CH_2 - CH(COOC_2H_5)_2 \longrightarrow$$



$$\longrightarrow NaBr + Br - CH_2 - CH_2 - \begin{array}{l} C(COOC_2H_5)_2 \\ | \\ CH_2 - CH_2 - CH_2 - CH(COOC_2H_5)_2. \end{array}$$

Of these reactions, I, II, III, IV and probably VI actually exist, as is shown by the research done by Perkin, Jr. [2] as well as by the above-mentioned work of Willstatter's.

The literature contains reports of a number of efforts to improve the yield of various products in the given reaction, such as, say, the cyclobutane-1,1-dicarboxylate [3,4] and the pentane-1,1,5,5-tetracarboxylate acid [5].

In the present investigation we endeavored to increase the yield of the γ-bromopropylmalonate; to this end we employed a procedure already used with success in an analogous reaction between sodium malonic ester and chlorobromotrimethylene, involving a change in the proportions of the reagents based on the law of mass action.

It has already been shown by Emil Fischer and Bergmann [6], as well as by B.A.Kazansky and the author of the present paper [7] that when a large excess of malonic ester is used, the reversible reaction between sodium malonic ester and the γ-chloropropylmalonate (a reaction similar to Reaction III above) can be shifted to the left:

$$NaCH(COOC_2H_5)_2 + ClCH_2 - CH_2 - CH_2 - CH(COOC_2H_5)_2 \rightleftarrows$$
$$\rightleftarrows CH_2(COOC_2H_5)_2 + ClCH_2 - CH_2 - CH_2CNa(COOC_2H_5)_2.$$

so that reactions like Reactions IV, V, and VI will no longer take place.

In this manner, we obtained the γ-chloropropylmalonate with a yield that was 76% of the theoretical by using three times the theoretical amount of malonic ester.

When trimethylene bromide replaces the chlorobromotrimethylene, the result changes fundamentally, as is shown by the experiments described below. Even using four times the theoretical amount of malonic ester, we did increase the yield of the γ-bromopropylmalonate, but only up to 36% of the theoretical value, which is still unsatisfactory, compared to the yield of the γ-chloropropylmalonate.

In this reaction a yield that is 60% of theory of the pentane-1,1,5,5-tetracarboxylate is obtained alongside the γ-bromopropylmalonate.

This difference in the behavior of trimethylene bromide and chlorobromotrimethylene in their reactions with sodium malonic ester will not appear unusual if we bear in mind the high reactivity of the bromine atom (compared to chlorine) in the γ-bromopropylmalonate. Therefore, the latter can react markedly with sodium malonic ester, which is why its end yield is so much lower than that of the γ-chloropropylmalonate.

To diminish the action of the γ-bromopropylmalonate upon sodium malonic ester and thus to eliminate Reaction II as far as possible, it is necessary — on the basis of the law of mass action — to increase the concentration of trimethylene bromide in the reaction mixture.

In fact, when 4 moles of trimethylene bromide and 4 moles of malonic ester were used in the reaction per gram atom of sodium, we obtained a yield of the γ-bromopropylmalonate that was 70.3% of theory, or almost three times the previous yield.

EXPERIMENTAL

The trimethylene bromide required was prepared by adding hydrogen bromide to allyl bromide by the Erlenmeyer method [8]. It boiled at 163-166° and had a

n_D^{13} 1.5260. The malonic ester distilled over in the temperature range of 193-195° and had a n_D^{12} 1.4248.

The reaction of trimethylene bromide with sodium malonic ester was effected in an apparatus consisting of a round-bottomed flask with a capacity of 0.75 liter, fitted with a mechanical stirrer, a reflux condenser, and a dropping funnel, which in turn was connected to a second reflux condenser through an adapter. Weighed quantities of trimethylene bromide and malonic ester were poured into the flask. The alcoholate was prepared right in the dropping funnel by adding metallic sodium to 20 times the amount of absolute alcohol. After the sodium had dissolved, the mechanical stirrer was started, and the alcoholate was added to the reaction mixture drop by drop as the solution was continuously stirred [9]. Then the mixture was stirred for one hour and heated for two hours on a boiling water bath. The reaction products were mixed with water, extracted with ether, and the ether extract twice washed with water and dried with calcined calcium chloride; the ether was then driven off, and the residue was subjected to fractional distillation in vacuum in a Vigret column 20 cm high.

Test 1. Taken: 41 g (0.2 mole) of trimethylene bromide, 128 g (0.8 mole) of malonic ester, and 4.7 g (0.2 gram atom) of metallic sodium.

Vaccum distillation yielded: 12 g of trimethylene bromide (fraction with a b.p. up to 75° at 20 mm), 90 g of malonic ester (fraction with b.p. of 85-94° at 16 mm), and 46 g of distillation residue.

The trimethylene bromide and malonic ester were again placed in the reaction with the addition of the spent amounts.

The test was repeated three times, and the combined residues were distilled in vacuum. Yield: 5.6 g of malonic ester (fraction up to 130° at 11 mm), 60.7 g of the γ-bromopropylmalonate (149-165° fraction at 11 mm), and 64.8 g of the pentane-1,1,5,5-tetracarboxylate (190-215° fraction at 12 mm).

The yield of the γ-bromopropylmalonate was 36% of theory (based on 0.6 mole as 100%); the yield of the pentane-1,1,5,5-tetracarboxylate was 60%.

Constants of γ-bromopropylmalonate: d_{20}^{20} 1.2860; n_D^{20} 1.4590.

$C_{10}H_{17}O_4Br$. MR calculated: 59.35.
MR found : 59.79

Test 2. Taken: 162 g of trimethylene bromide (0.8 moles), 128 g (0.8 mole) of malonic ester, and 4.7 g (0.2 gram atom) of metallic sodium.

Upon distillation of the reaction products in vacuum there were obtained (average of three runs): 125 g of trimethylene bromide (fraction up to 73° at 18 mm), 90 g of malonic ester (90-96° at 18 mm), and a distillation residue of 52.8 g.

The combined residues of three tests yielded upon vacuum distillation: 12.2 g of malonic ester (fraction up to 130° at 10 mm), 118.6 g of the γ-bromopropylmalonate (149-160° fraction at 10 mm), and 16.7 g of the pentane-1,1,5,5-tetracarboxylate.

The yield of the γ-bromopropylmalonate was 70.3% of theory, and the yield of the pentane-1,1,5,5-tetracarboxylate was 15.4%. Upon repeated distillation the γ-bromopropylmalonate boiled at 150-155° at 10 mm.

Product constants: d_{20}^{20} 1.2856; n_D^{20} 1.4594.

$C_{10}H_{17}O_4Br$. Calculated MR: 59.35.
Found MR: 59.79.

SUMMARY

The following conclusions may be reached from the experiments performed:

The negligible yield of the γ-bromopropylmalonate formed in the initial phase of the reaction between trimethylene bromide and sodium malonic ester is due to a number of side reactions.

The law of mass action indicates that large excesses of malonic ester and trimethylene bromide must be used to increase the yield of the γ-bromopropylmalonate.

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SYNTHESIS OF THE AMINOSULFONES

IV. PREPARATION OF 4-NITROPHENYL-6'-(2'-AMINO-4'-METHYL-PYRIMIDYL) SULFIDE AND SOME OF ITS DERIVATIVES

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Feldman, Khikhshau, and Mann [1] have reported that 4-amino-phenyl-2'-aminothiazole-5'-sulfone (promizole) are highly active when tested on guinea pigs infected with tuberculosis.

As promizole (II) is the sulfone isostere of sulfathiazole (I), the synthesis of other isosteres of the sulfamides naturally aroused interest.

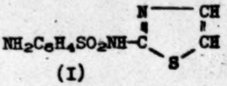
The present paper announces the synthesis of an acetyl derivative of an isostere of sulfamerazine (III,IV) and of some compounds closely related to it, obtained from 4-nitro-phenyl-6'-(2'-amino-4'-methyl-pyrimidyl) sulfide.

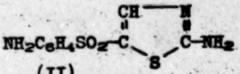
(See page a 114)

The initial products for the synthesis of 4-nitrophenyl-6'-(2'-amino-4'-methyl-pyrimidyl) sulfide were p-nitrophenylmercaptan and 2-amino-4-methyl-6-chloropyrimidine. p-Nitrophenylmercaptan was prepared from p-nitrochlorobenzene by the Zincke and Lenhard method [2] with slight modifications; 2-amino-4-methyl 6-chloropyrimidine was synthesized by the method described in the literature [3]. Guanidine thiocyanate, condensed with acetoacetic ester, yielded -- after washing with alcohol - a 2-amino-4-methyl-6 hydroxy pyrimidine that was suitable for further operations; the compound was converted into 2-amino-4-methyl-6-chloro-pyrimidine by phosphorus oxychloride, with a yield of 90%.

Endeavors to condense 2-amino-4-methyl-6-chloropyrimidine with the silver salt of p-acetaminophenyl-sulfinic acid, with a view toward obtaining the sulfonic derivative directly, were fruitless, despite a number of changes made in the reaction conditions (temperature, solvent, etc.,). Success was had in condensing 2-amino-4-methyl-6-chloropyrimidine with p-nitrophenylpotassium mercaptide (cf. V, Diagram 1).

When 4-nitrophenyl-6'-(2'-acetylamino-4'-methyl-pyrimidyl) sulfide is oxidized to the corresponding sulfone (VII, VIII), some difficulty is encountered. If this is done with too weak hydrogen peroxide in glacial acetic acid at a


(I)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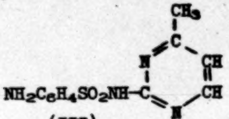

(III)

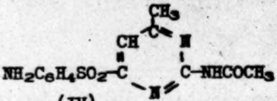
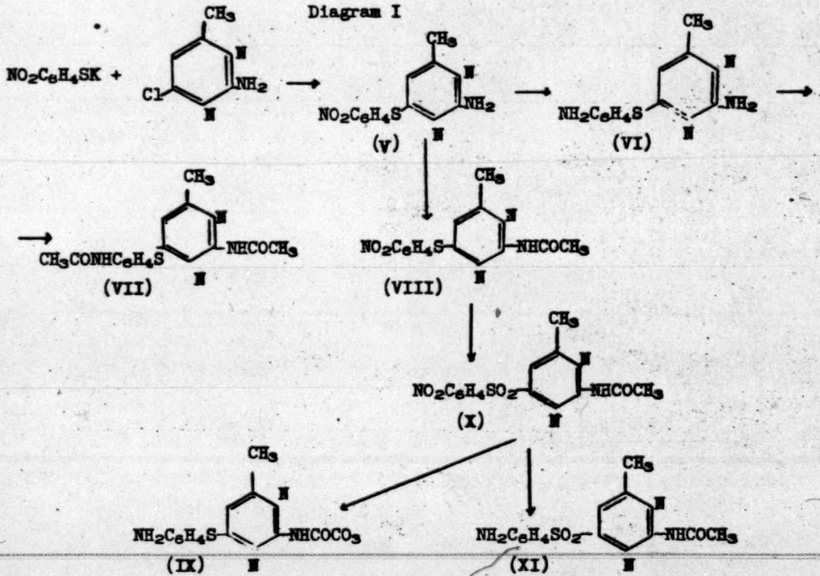

(IV)

Diagram I



temperature of 65-70°, the acetyl group is partially saponified and the initial product is regained. At temperatures above 85°, oxidation by concentrated hydrogen peroxide (28-30%) in glacial acetic acid results in breaking up the initial sulfide. Among the products of the reaction we have identified dinitrodiphenyl disulfide and substances containing no sulfur.

Under the conditions of our experiment 4-nitrophenyl-6'-(2'-acetylamino--4'methyl-pyrimidyl) sulfone (VIII) proved to be a compound that is quite unstable in the presence of alkalis, as well as in the presence of acids at higher temperatures.

In a mixture of glacial acetic acid and 6N hydrochloric acid at a temperature of 75-80° the acetyl group did not saponify during five hours, nor did heating to 105° for two hours yield any saponification products, but the molecule broke down after the lapse of 3 or 5 hours. The breakdown of the molecule occurred at 50-55° in a 10% solution of caustic soda.

Efforts to reduce the 4-nitrophenyl-6'-(2'-acetylamino-4'-methyl-pyrimidyl) sulfone indicated that the reduced product was even more unstable, especially at higher temperatures. When it was heated to 60-65° for four hours with reduced iron in a neutral medium, a substance was isolated that contained no sulfur.

Efforts to reduce this nitrosulfone with molecular hydrogen at room temperature in the presence of a Rainey nickel catalyst yielded a product with a m.p. of 190-194° (about 10° higher than its true melting point). Endeavors to crystallize the substance obtained from absolute ethyl alcohol yielded a mixture with a still higher melting point: analyses of the substances with m.p. of 190-194°, 194-197°, and 207-210° indicated that these mixtures contained molecular cleavage products. Experiments were set up to effect the reduction of 4-nitrophenyl-6'-(2'-acetylamino-4'-methyl-pyrimidyl) sulfone with a platinum catalyst, as used by Adams, prepared as usual at 500-550°. It proved to be too active for this nitrosulfone. It produced a mixture, whose analysis showed that it also contained products that had no sulfur. Reduction of this nitrosulfone succeeds only with a less active platinum catalyst, prepared at a temperature of 360-390°.

EXPERIMENTAL

4-Nitrophenyl-6'-(2'-amino-4'-methyl-pyrimidyl) sulfide (V)

Into a round-bottomed flask fitted with a condenser and a stirrer there were placed 39 g (0.27 gram molecule) of 2-amino-4-methyl-6-chloropyrimidine, 31 g (0.2 gram molecule) of p-nitrophenylthiol, and 8 g (0.32 gram molecule) of caustic potash dissolved in 300 ml of ethyl alcohol. The mixture was heated, with constant stirring, over a water bath for 4-5 hours at the boiling temperature of the mass. The yellow deposit that settled out upon cooling was filtered out and washed with cold water until no potassium mercaptide could be found in the wash water. After drying, the deposit was washed several times with hot acetone. Yield: 50 g (70.5%).

The sulfide obtained constituted a finely crystalline substance with a m.p. of 214-215°; it could be used for subsequent acetylation without further purification. It crystallized out of acetic acid and benzene; the sulfide dissolved with difficulty in the latter. Melting point of the crystallized product was 216-217°. Upon heating it dissolved in methanol, acetone, and chloroform, and – with difficulty – in ethyl alcohol.

Found %: N 21.37; S 12.21.
$C_{11}H_{10}O_2N_4S$. Calculated %: N 21.11; S 12.33.

4-Aminophenyl-6'-(2'-amino-4'-methyl-pyrimidyl) sulfide (VI)

Reduction with iron in a neutral medium. In a three-necked flask fitted with a rapid stirrer there was placed a solution of 0.65 g of ammonium chloride in 65 ml of water. At a temperature of 60-65° 4 g of reduced iron was added, after which 3 g of 4-nitrophenyl-6'-(2'-amino-4'-methyl-pyrimidyl) sulfide was gradually added. The reaction mass was kept at this temperature for 4 hours with constant stirring. After conclusion of the reaction and cooling of the mixture the sludge was drawn off and leached out with acetone. The acetone extract was dried over calcined potash, filtered, and distilled in vacuum. We obtained 1.7 g (65%) of a product, which had a m.p. of 200-202° after being crystallized from ethyl alcohol. The diaminosulfide was easily soluble in the usual organic solvents.

Found %: N 23.83; S 13.35.
$C_{11}H_{12}N_4S$. Calculated %: N 24.14; S 13.79.

Reduction with hydrogen in the presence of a Rainey nickel catalyst. 4 g of the nitrosulfide, 130 ml of ethyl alcohol, and 8 g of Rainey nickel catalyst were shaken up in a vessel for hydrogenation in a stream of hydrogen at room temperature and atmospheric pressure. After the theoretically required amount of hydrogen had been absorbed, the reaction mass was filtered to remove the catalyst, and the alcohol was driven off in vacuum. We obtained 2.9 g of a white crystalline deposit (83% yield). It had a m.p. of 200-201° after crystallization from absolute ethyl alcohol. No depression of the melting point was observed when it was mixed with the substance obtained by reduction with iron in a neutral medium.

4-Acetylaminophenyl-6'-(2'-acetylamino-4'-methyl-pyrimidyl) sulfide (VII)

In a round-bottomed flask fitted with a reflux condenser 2 g of 4-aminophenyl-6'-(2'-amino-4'-methyl-pyrimidyl) sulfide (VI) in 15 ml of acetic anhydride were heated for four hours. After cooling, a substance that was subsequently filtered out and washed with ether was isolated from the filtered solution. Yield 1.3 g. Its m.p. was 229-231° after crystallization from anhydrous methanol. The 4-acetylaminophenyl-6'-(2'-acetylamino-4'-methyl-pyrimidyl) sulfide (VII) prepared dissolves upon heating in ethyl alcohol and methanol, but is insoluble in water, acetone, ether, and benzene.

Found %: N 17.70; S 9.62.
$C_{15}H_{16}O_2N_4S$. Calculated %: N 17.72; S 10.10.

4-Nitrophenyl-6'-(2'-acetylamino-4'-methyl-pyrimidyl) sulfide (VIII)

50 g of 4-nitrophenyl-6'-(2'-amino-4'-methyl-pyrimidyl) sulfide was heated for four hours with 250 ml of redistilled acetic anhydride in a round-bottomed flask fitted with a reflux condenser over a water bath. The hot solution was filtered to free it of contaminations, and the deposit that settled out after cooling was drawn off and washed with methanol. Yield: 27.5 g (46.2%) of the acetyl sulfide with a m.p. of 177-179°. After the acetic anhydride had been driven off from the mother liquor by distillation in vacuum, we obtained 27.6 g of a product with a m.p. of 164-171°, which was reacetylated under the conditions described. This yielded an additional 11.4 g with a m.p. of 176-178°. Aggregate yield: 68%. The product crystallized from methanol had a m.p. of 177-179°. It is soluble at room temperature in acetone, and upon heating in ethyl alcohol and benzene. It is insoluble in water.

Found %: C 51.54; H 3.87; N 18.58; S 10.70.
$C_{10}H_{12}O_2N_4S$. Calculated %: C 51.32; H 3.95; N 18.42; S 10.53.

4-Amino-6'-(2'-acetylamino-4'-methyl-pyrimidyl) sulfide (IX)

In a three-necked flask fitted with a reflux condenser and a rapid stirrer there was placed a solution of 1 g of ammonium chloride in 100 ml of water. At

60° there was placed in the flask 6.5 g of reduced iron, after which 5 g of 4-nitrophenyl-6'(2'-acetylamino-4'-methyl-pyrimidyl) sulfide (VIII) was gradually added at the same temperature.

Heating and stirring of the reaction mixture at the same temperature were continued for 4 hours. After the reaction was concluded and the mixture had cooled, it was drawn up into a Buchner funnel, and the sludge was extracted with methanol. The dried alcoholic solution was distilled in vacuum. Anhydrous ether was added to the oily liquid that remained behind after vacuum distillation, and 3.4 g (67%) of a crystalline product was then isolated.

After being recrystallized twice from absolute alcohol the 4-aminophenyl-6'-(2'-acetylamino-4'-methyl-pyrimidyl) sulfide (IX) melted at 164-166°.

It is soluble in acetone, methanol, and ethyl alcohol. It is insoluble in water or ether.

Found %: S 11.68.
$C_{13}H_{14}ON_4S$. Calculated %: S 11.67.

4-Nitrophenyl-6'-(2'-acetylamino-4'-methyl-pyrimidyl) sulfone (X)

Into a three-necked flask, fitted with a reflux condenser, a stirrer, a thermometer, and a dropping funnel, there were poured 26 g of 4-nitrophenyl--6'-(2'-acetylamino-4'-methyl-pyrimidyl) sulfide (IX), 50 g of acetic anhydride, and 150 ml of glacial acetic acid. Upon heating to 65° over a water bath with constant stirring, all the acetyl sulfide entered solution. At 45-50° 52 ml of 24% hydrogen peroxide (0.36 mole) was added to the contents of the flask from a dropping funnel. As this resulted in a rise of temperature, the reaction mass was cooled. After all the hydrogen peroxide had been added, the reaction solution was heated to 75-80° for 5 hours. The solution was then filtered free of impurities, and the acetic acid was driven off in vacuum; the residue left after distillation was decanted into a porcelain dish. The crystallizing deposit was sucked up into a Buchner funnel and washed with methanol. We obtained 16 g (57% of theory) of a substance, which had a m.p. of 239-241° after recrystallization from methanol. The acetyl sulfone consists of prismatic crystals soluble in water. Upon heating they also dissolve in methanol and ethyl alcohol.

Found %: N 16.51; S 9.61.
$C_{13}H_{14}O_5N_4S$. Calculated %: N 16.60; S 9.52.

Saponification Tests of 4-Nitrophenyl-6'-(2'-acetyl-amino-4'--pyrimidyl) sulfone (X)

a) Into a round-bottomed flask fitted with a reflux condenser there were poured 2 g of 4-nitrophenyl-6'-(2'-acetylamino-4'-methyl-pyrimidyl) sulfone mixed together with 12 ml of glacial acetic acid and 46 ml of 50% sulfuric acid. The solution was heated to 70-75° for 5 hours. After conclusion of the reaction there settled out of the solution a deposit that had a m.p. of 274-276°, after cooling, neutralization with spirits of ammonia, and recrystallization from absolute alcohol. This substance contained no sulfur and was nothing but 2-amino-4-methyl-6-hydroxypyrimidine.

b) 1 g of the acetyl sulfone was heated to 50-55° for 2 hours with 10 ml of 10% NaOH. Upon cooling dilute hydrochloric acid was added to the reaction solution until a neutral litmus-paper reaction was obtained. After the solution had been reduced to 1/3 by vacuum evaporation sodium chloride was thrown down.

Upon further evaporation the same deposit settled out that was obtained in Test (a) and contained no sulfur (but was merely contaminated somewhat with sodium chloride.)

4-Aminophenyl-6'-(2'-acetylamino-4'-methyl-pyrimidyl) sulfone (XI)

a) Reduction of 4-nitrophenyl-6'-(2'-acetylamino-4'-methyl-pyrimidyl) sulfone (X) iron in a neutral medium. Into a three-necked flask, fitted with a reflux condenser and a rapid stirrer, there was poured a solution of 0.45 g of ammonium chloride in 45 ml of water. At 60-65° there was placed in the flask 2.5 g of reduced iron, after which 2 g of 4-nitrophenyl-6'-(2'-acetylamino-4'-methyl-pyrimidyl) sulfone was gradually added to the reaction mass at the same temperature. Heating was continued at this temperature for 4 hours. After the reaction was ended, the mixture was cooled and then drawn up into a Buchner funnel. The sludge was extracted with alcohol; after the latter had been driven off, we obtained a product that contained no sulfur and had a m.p. of 280-285°. The m.p. was 284-286° after crystallization, i.e., it was none other than 2-amino-4-methyl-6-hydroxypyrimidine.

b) Reduction of 4-nitrophenyl-6'-(2'-acetylamino-4'-methyl-pyrimidyl) sulfone (X) by a platinum catalyst. 2 g of the nitrosulfone were dissolved in 320 ml of ethyl alcohol. To the solution there was added 0.035 g of freshly prepared low-activity platinum catalyst. Catalysis lasted 4-6 hours. After the theoretically required amount of hydrogen had been absorbed, the filtered solution was driven off in vacuum at a bath temperature of 25°. The deposit that settled out (1.6 g) was drawn up and recrystallized from 90% alcohol. The crystalline product was light cream in color; it fused at 182-185° in a previously warmed vessel.

The aminosulfone is easily soluble in water, and upon heating it also dissolves in ethyl alcohol and methanol. It is insoluble in other organic solvents.

Found %: N 18.33; S 10.09.
$C_{13}H_{14}N_4SO_3$. Calculated %: N 18.36; S 10.49.

4-Meconyl-aminophenol-6'-(2'-amino-4'-methyl pyrimidyl) sulfide (XII)

Into a three-necked flask, fitted with a reflux condenser and a stirrer, there were poured 2 g of 4-aminophenyl-6'-(2'-amino-4'-methyl-pyrimidyl) sulfide, 1.8 g of opianic acid, and 80 ml of ethyl acetate. The mixture was heated to 60° with constant stirring. At first everything dissolved, but later on a deposit gradually settled out. The temperature was then raised to 80°, and the reaction continued for 3 hours. After the reaction mixture had cooled, the deposit was drawn up and washed with hot alcohol and ether. A white crystalline deposit was obtained after purification.

Weight: 3.5 g; m.p. 173-175°.

Found %: C 59.70; H 4.93; N 12.70.
$C_{21}H_{20}O_4N_4S$. Calculated %: C 59.43; H 4.71; N 12.66.

SUMMARY

1. 4-Nitrophenyl-6'-(2'-amino-4'-methyl-pyrimidyl) sulfide was obtained by the condensation of p-nitrophenylpotassium mercaptide with 2-amino-4-methyl-6-chloropyrimidine; from it a number of derivates were synthesized.

2. A number of compounds proved to be quite unstable to alkalis, as well as to acids at higher temperatures; the molecule is hydrolyzed, 4-methyl-2-hydroxypyrimidine separating out.

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DERIVATIVES OF 4-DIETHYLAMINOALKYLAMINOQUINOLINE

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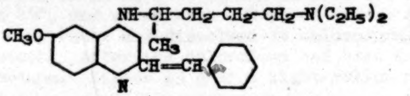
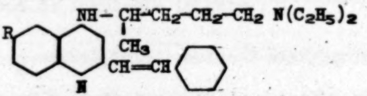
In our previous paper [1] we reported the synthesis of 6-methoxy-4-diethyl-aminoisopentylamino-2-styrylquinoline·

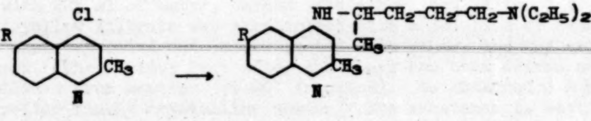


No compounds of this structure have been described in the literature, which is why it was thought advisable to subject this series to more extensive chemical and chemotherapeutical investigation. With this in mind we synthesized some new derivatives of styrylquinoline with the following general formula:



(I) R = H; (II) R = OC_2H_5; (III) R = $NHCOCH_3$.

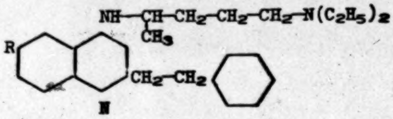
The corresponding 4-chloroquinaldines served as the initial products; upon reacting them with 1-diethyl-4-aminopentane they are converted into 4-diethylaminoisopentylamino derivatives of quinaldine:



Condensation of the latter with benzaldehyde in the presence of piperidine results in the formation of the corresponding styrylquinolines.

The compounds synthesized constitute light-yellow crystalline substances, easily soluble in water, as dihydrochlorides.

Hydrogenation of the styrylquinolines in the presence of Pd results in the formation of 2-(β-phenylethyl) derivatives of the following general formula:



(IV) R = OCH_3; (V) R = OC_2H_5; (VI) R = H.

These compounds differ from the styrylquinolines in being colorless crystalline substances.

EXPERIMENTAL

4-(δ-Diethylamino-α-methylbutyl)-aminoquinaldine

A mixture of 19 g of 4-chloroquinaldine and 30 g of 1-diethylamino-4-aminopentane was heated for 10 hours over an oil bath at 190-200°. The reaction mass was then cooled to 80°, and mixed with 200 ml of water; the thick oil that formed was washed with water and dissolved in chloroform, and the solution was then dried with potash. After the chloroform had been driven off, the residue was distilled in vacuum. Yield: 15 g of a light-yellow oil, boiling at 200-201° at 5 mm.

0.1086 g substance: 13.45 ml N_2 (22°, 748 mm)
Found %: N 13.74
$C_{19}H_{29}N_3$. Calculated %: N 14.04.

The substance dissolves easily in the ordinary organic solvents and in dilute mineral acids, but is insoluble in water.

4-(δ-Diethylamino-α-methyl-butyl)-amino-2-styrylquinoline (I)

A mixture of 14 g of 4-(δ-diethylamino-α-methylbutyl)-aminoquinaldine, 30 g of benzaldehyde, and 1 g of piperidine was heated for 7 hours over an oil bath at 155-160°. The dark-brown mass obtained was dissolved in 150 ml of ether, and the base was extracted three times from the ether extract by 10% hydrochloric acid, using 25 ml of acid each time. The hydrochloric-acid solution was diluted with 225 ml of water, washed with ether, and filtered free of the sludge. The light-yellow filtrate was alkalinized with a solution of caustic soda, and the base that separated out was extracted with ether, and the extract was dried with potash. The residue left after the ether had been driven off was twice recrystallized from benzine (70-90° fraction). We obtained 8 g of substance as a light-yellow finely crystalline powder. The substance is easily soluble in alcohol, ether, chloroform, and hot benzine. M.p. 109-110°.

3.361 mg substance: 9.894 mg CO_2; 2.670 mg H_2O.
3.049 mg substance: 0.301 ml N_2 (17.5°, 722 mm).
Found %: C 80.28; H 8.89; N 11.03.
$C_{26}H_{33}N_3$. Calculated %: C 80.56; H 8.59; N 10.85.

6-Ethoxy-4-(δ-diethylamino-α-methylbutyl)-aminoquinaldine

A mixture of 15 g of 6-ethoxy-4-chloroquinaldine and 30 g of 1-diethylamino-4-aminopentane was heated on an oil bath to 185-190° for 8 hours. The reaction mass was then mixed with 200 ml of water and allowed to stand for 48 hours at 0°. The congealed mass was separated from the water and twice recrystallized from five times its weight of ether. We obtained 9.5 g of a substance constituting a white crystalline powder with a m.p. of 107-108°. The substance is easily soluble in alcohol and chloroform and also dissolves in ether.

Kjeldahl Nitrogen Determination:

0.3870 g substance consumed: 34.5 ml 0.1 N HCl.
Found %: N 12.48.
$C_{21}H_{33}ON_3$. Calculated %: N 12.24.

6-Ethoxy-4-(δ-Diethylamino-α-methylbutyl)-amino-2-styrylquinoline (II)

A mixture of 7 g of 6-ethoxy-4-(δ-diethylamino-α-metnylbutyl)aminoquinaldine, 14 g of benzaldehyde, and 1 g of piperidine was heated on an oil bath to 160-165° for 5 hours. The thick dark-brown mass that formed was mixed with 70 ml of ether and set aside to stand for 12 hours at 0°. The yellow crystals that separated out were filtered out, washed with ether, and dried. Yield: 3 g; m.p. 124-125°. The ether filtrate was extracted three times with 10% hydrochloric acid, using 25 ml of the acid each time, and the hydrochloric-acid extract was washed with ether and alkalinized with a 40% solution of caustic soda, the oil that separated out being again extracted with ether and the extract dried with potash. When the ether solution was concentrated to a volume of 25 ml, 3 g of light-yellow crystals with a m.p. of 132-137° settled out. Purifying the substance by repeated recrystallization from ether or benzine is unsatisfactory, involving considerable losses. Purifying the substance as a hydrochloride was found to be much more effective. The base was dissolved with heating in 30 ml of 17% hydrochloric acid and left to cool, being stirred continuously. The styrylquinoline hydrochloride separated was filtered out, washed with 17% hydrochloric acid, and converted into a base which was then recrystallized from benzine (70-90° fraction).

We obtained 2 g of substance as a light-yellow crystalline powder with a m.p. of 144-145°. The substance is easily soluble in alcohol, and chloroform; it is soluble in ether, and moderately soluble in benzine.

3.791 mg substance: 10.830 mg CO_2; 2.881 mg H_2O.
2.955 mg substance: 0.255 ml N_2 (18°, 746 mm).
Found %: C 77.91; H 8.50; N 9.95.
$C_{28}H_{37}ON_3$. Calculated %: C 77.90; H 8.65; N 9.74.

The substance prepared above, with a m.p. of 124-125°, does not experience a change in melting point when recrystallized from acetone. Upon analysis it was found to be the dibenzoate of 6-ethoxy-4-diethylaminoisopentantylamino-2-styrylquinoline.

Kjeldahl Nitrogen Determination:

0.850 g substance consumed: 3.88 ml 0.1 N HCl.
Found %: N 6.39.
$C_{28}H_{37}ON_3 \cdot 2C_6H_5COOH$. Calculated %: N 6.22.

When this substance is decomposed by an alkali a base is isolated that melts at 144-145° after recrystallization from benzine.

6-Acetamino-4-(δ-diethylamino-α-methylbutyl)-aminoquinaldine

A mixture of 16 g of 6-acetamino-4-chloroquinaldine and 40 g of 1-diethylamino-4-aminopentane was heated over an oil bath to 190-200° for 8 hours. The reaction mass was mixed with 300 ml of water, and the oil that separated out was extracted with ether, the extract being dried with potash. After the ether had been driven off, there remained a viscous oil, which was repeatedly washed with benzine (70-90°) and then dissolved in 50 ml of ether and set aside to stand for 48 hours at 0°. The crystalline deposit that settled out was filtered out, washed with ether, and dried. We obtained 5 g of a substance with a m.p. of 109-115°. The melting point rose to 137°-138° after recrystallization from 6 ml of acetone. Yield: 3 g. The substance dissolves well in alcohol, chloroform, and acetone, and poorly in ether and benzine.

0.1098 g substance: 15.4 ml N_2 (25°, 750 mm).
Found %: N 15.4
$C_{21}H_{32}ON_4$. Calculated %: N 15.7

6-Acetamino-4-(δ-diethylamino-α-methylbutylamino)-2-styrylquinoline (III)

A mixture of 5 g of 6-acetamino-4-(δ-diethylamino-α-methylbutyl)-aminoquinoline, 10 g of benzaldehyde, and 0.5 g of piperidine was heated for 6 hours on an oil bath to 150-155°. The viscous brown mass that formed was dissolved in ether, and the ether solution was extracted with 30 ml of 5% hydrochloric acid. The hydrochloric-acid solution was diluted with water until no more sludge formed, filtered, and alkalinized with a 10% solution of caustic soda, the base that separated out being extracted with ether. The ether extract was dried with potash, the ether driven off, and the residue -- a mixture of a crystalline powder and an oil -- was washed with a small quantity of ether to eliminate the oily impurities. After double recrystallization of the residue from seven times its weight of ether, we obtained 0.7 g of a light-yellow crystalline powder that fused at 139-140°. The substance dissolved easily in alcohol, acetone, and chloroform, and with more difficulty in ether and benzine.

0.0984 mg substance: 11.3 ml N_2 (22°, 751 mm)
Found %: N 12.79.
$C_{28}H_{36}ON_4$. Calculated %: N 12.61.

6-Methoxy-4-(δ-diethylamino-α-methylbutyl)-amino-2-(β-phenylethyl)-quinoline (IV).

To a solution of 2 g of 6-methoxy-4-(δ-diethylamino-α-methylbutyl)-amino-2-styrylquinoline hydrochloride in 60 ml of water there was added 2 ml of a 2% solution of palladium chloride, and the mixture was subjected to hydrogenation at room temperature under a pressure of 50-60 cm of water column. Hydrogenation was continued for several hours. After the computed quantity of hydrogen had been absorbed, the catalyst was filtered out, the filtrate alkalinized with caustic soda, the base formed extracted with ether, and the extract dried with potash. Driving off the ether left behind 1.43 g of a transparent, colorless viscous oil, which slowly crystallized upon standing above caustic potash in a exsiccator. After recrystallization from benzine (70-90°) the substance was obtained as snow-white crystals (microscopic nodes of needles). It dissolves easily in alcohol, ether, acetone, and hot benzine; m.p. 85-86°.

3.599 mg substance: 10.132 mg CO_2; 2.890 mg H_2O.
2.636 mg substance: 0.237 ml N_2 (19.5°, 737.5 mm).
Found %: C 76.78; H 8.98; N 10.16.
$C_{27}H_{37}ON_3$. Calculated %: C 77.27; H 8.89; N 10.02.

6-Ethoxy-4-(δ-diethylamino-α-methylbutyl)-amino-2-(β-phenylethyl)-quinoline (V)

To a solution of 2.15 g of 6-ethoxy-4-(δ-diethylamino-α-methylbutyl)-amino-2-styrylquinoline in 100 ml of 0.2 N hydrochloric acid there was added 8 ml of a 2% solution of palladium chloride. A yellow deposit was thrown down, which did not dissolve upon shaking. The mixture was hydrogenated for several hours at room temperature. After hydrogenation was complete, the solution was filtered to remove the catalyst and treated with alkali; the base formed was extracted with ether, and the ether extract dried with potash. After removal of the ether, what remained was an almost colorless viscous oil that crystallized upon standing. After recrystallization from benzine (70-90°) we got a white crystalline powder with a m.p. of 102-103°. The substance dissolves easily in alcohol, ether, acetone, chloroform, and hot benzine.

4.496 mg substance: 12.819 mg CO_2; 3.581 ml H_2O.
4.942 mg substance: 0.430 ml N_2 (18°, 738.5 mm).
Found %: C 77.76; H 8.91; N 9.92.
$C_{28}H_{39}ON_3$. Calculated %: C 77.54; H 9.07; N 9.69.

4-(δ-Diethylamino-α-methylbutyl)-amino-2-(β-phenylethyl)-quinoline (VI)

This compound was synthesized under the conditions described in the preceding experiment. It is a white crystalline powder (from benzine) that is easily soluble in alcohol, ether, acetone, and hot benzine. M.p. 82-83°.

3.429 mg substance: 10.062 mg CO_2; 2.769 mg H_2O.
3.291 mg substance: 0.313 ml N_2 (21.5°, 737 mm).
Found %: C 80.03; H 9.04; N 10.70.
$C_{26}H_{35}N_3$. Calculated %: C 80.02; H 9.06; N 10.79.

SUMMARY

The synthesis of derivatives of 4-diethylaminoisopentylaminoquinoline, involving attaching a styryl or β-phenylethyl group at position 2 of the quinoline ring and an alkoxy or acetamino group at position 6, was achieved.

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RESEARCH ON THE POLYMERIZATION OF ALLYL ACRYLATE

I. DETERMINING THE STRUCTURE AND MOLECULAR WEIGHT OF SOLUBLE FORMS OF POLYALLYL ACRYLATE

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It has been shown by various authors that allyl acrylate and analogous compounds, possessing two unconjugated double bonds, form spatial (three-dimensional, latticed) polymers that are insoluble in ordinary solvents; this is true both of the individual compounds and of copolymerization with other unsaturated compounds. In the early stages of the polymerization process a soluble polymer is formed, which is then converted into the insoluble form [1,2,3]. The soluble form of the polymer of allyl methacrylate can be produced by the action of benzoyl peroxide irradiated by ultraviolet light [4]. We discovered that when allyl acrylate is polymerized by the action of benzoyl peroxide in dilute solutions (concentration of the monomer up to 6% w/w), a polymer is formed throughout the process that is very easily soluble in benzene, chloroform, carbon tetrachloride, acetone, and glacial acetic acid, but is insoluble in methanol and ethyl alcohol. Data are reported in this paper that characterize the structure and molecular weight of the soluble form of polyallyl acrylate.

EXPERIMENTAL

Initial Products

Allyl acrylate was synthesized by direct esterification as well as by the method of re-esterification [1]. The product was purified by double distillation in a stream of nitrogen. Its constants are:

$$n_D^{20}\ 1.4330;\quad d_4^{20}\ 0.9333;\quad d_4^{60}\ 0.888.$$
$$\text{B.p. } 119.5\text{-}121.5^\circ\ (750\ \text{mm}).$$

The benzene employed as a solvent was purified in the usual manner by agitation with concentrated H_2SO_4 and metallic mercury, followed by distillation over metallic sodium.

The benzoyl peroxide was purified by precipitation by methanol from a chloroform solution, followed by washing the precipitate and evacuation in vacuum until constant weight is attained. The purified peroxide was 99.8% pure.

Apparatus and Methods of Polymerization

We selected the dilatometric method, which enabled us to study the kinetics of the process besides making it possible to prepare the quantity of polymer required for investigating its structure and determining its molecular weight.

The experiments were performed in glass dilatometers, fitted with capillaries 1-2 mm in diameter. The necessary amount of benzoyl peroxide was first placed in the dilatometers, after which they were sealed to the apparatus destined to receive the reaction mixture (Fig. 1).

The allyl acrylate was kept in trap 1, which was kept constantly chilled during intervals between runs. The amount of allyl acrylate required for a test was condensed over from trap 1 to ampoule 2, provided with graduations, from which the monomer was in turn condensed into dilatometer 3.

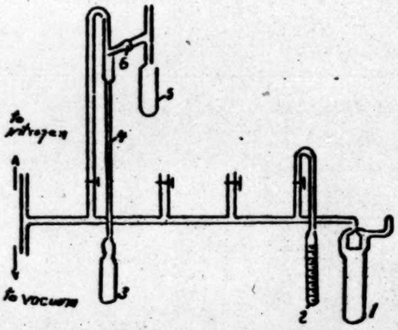

Fig. 1. Apparatus layout

The benzene was introduced with the nitrogen counterflow, freed from traces of oxygen, into ampoule 5, after which the ampoule's upper tube was sealed. The system was evacuated, and the benzene was poured into dilatometer 3 by turning ampoule 5 about its ground-glass joint 6. The system was then filled with nitrogen and the dilatometer was sealed off. The apparatus layout made it possible to fill several dilatometers at the same time.

The reaction was carried out in a water thermostat at a temperature of 60° ± 0.2°.

When the required depth of transformation was achieved, the dilatometer was opened and its contents transferred quantitatively to a measuring flask.

The concept of depth (percentage) of polymerization, determined dilatometrically, was likewise checked gravimetrically; this was done by subjecting a measured quantity of the solution in the measuring flask to evacuation in vacuo until constant weight is reached. In some cases the depth of polymerization was also determined by the method of reprecipitating the polymer with methanol or ethyl alcohol from a benzene solution, followed by drying the precipitate until its weight remained constant. The results obtained by all three methods were in good agreement.

To calculate the depth of polymerization in the dilatometric experiments, we first found the compression coefficient of allyl acrylate during polymerization. It was established that the change in the specific volume of allyl acrylate during polymerization is:

$$\frac{1}{d_{mon.}} - \frac{1}{d_{pol.}} = 0.287, \qquad (1)$$

when a soluble form of the polymer is formed (60°), where $d_{mon.}$ = specific gravity of the monomer; $d_{pol.}$ = specific gravity of the polymer.

As the weight of the polymer formed, g, is related to the general change in volume of the system during polymerization, Δv, by the equation:

$$g = \frac{\Delta v}{\frac{1}{d_{mon}} - \frac{1}{d_{pol.}}} \qquad (2)$$

in our case

$$g = 3.49\ \Delta v,$$

where g = polymer weight, in grams; Δv = change in volume of the system, in ml.

Method of Determining the Structure of the Polymer

Samples of the polymer were prepared for analysis in the following manner: the polymer was precipitated from a benzene solution by five times its volume of ethyl alcohol or methanol; the solution was then chilled with ice for half an hour, after which the polymer deposit was filtered out on a paper filter, washed repeatedly with alcohol, and evacuated in vacuum at room temperature to constant weight. After this treatment the polymer contained no traces of benzoyl peroxide, the monomer, or the solvent.

To determine the polymer structure we first thought of using the method of saponifying the polymer with alkali, followed by analysis of the low-molecular products of saponification. The method of selective bromination turned out to be simpler and more accurate, however.

When a molecule of allyl acrylate is added to a linear polymer chain, three types of structures may be formed: "acrylic bond" polymerization (I); "allyl bond" polymerization (II); and a mixed type of polymerization (III).

It is quite understandable that determination of the structure of the side chains provides complete information on which of the monomer's double bonds serves in the formation of the basic polymer chain.

To discover the "acrylic" and "allyl" double bonds in the polymer's side chains we made use of the different readiness of these two types of bonds to enter into the bromine-addition reaction.

When the bromide-bromate method is used, the "allyl" double bond is brominated quantitatively, whereas the "acrylic" bond is practically not brominated at all in certain solvents. (This circumstance may be demonstrated by the bromination of allyl alcohol or allyl acetate in an acetic-acid medium, these compounds being brominated quantitatively, as against methyl acrylate, say, only 2-3% of which is brominated, as we have been able to prove.)

We established that the bromide-bromate method, together with the employment of $HgSO_4$ as a catalyst [5], may be used successfully for the separate determination of the ''allyl" and "acrylic" double bonds in analyzable form. In working out the operating procedures we paid special attention to keeping all the polymer in solution during bromination and to keeping the reaction mixture homogeneous.

The procedure worked out by us is as follows:

Determination of " Allyl" Double Bonds

A weighed amount of the polymer, 0.05-0.06 g, was dissolved in 10.0 ml of CCl_4 and 40.0 ml of glacial CH_3COOH, and 5.0 ml of 0.2 N bromide-bromate solution was added. The mixture was allowed to stand in the dark for 60 minutes. Then 20.0 ml of a 10% solution of H_2SO_4 and 3 ml of a saturated solution of KI were added, and the I_2 that separates out was titrated with a solution of $NA_2S_2O_3$. A control was run at the same time.

Determining Overall Unsaturation

A weighed amount of the polymer, 0.05-0.06 g, was dissolved in 10.0 ml of CCl_4, and 60.0 ml of glacial CH_3COOH, and 5.0 of 0.2 N bromide-bromate solution was added. The mixture was allowed to stand in the dark for 60 minutes. Then 7.5 ml of a 0.2 molar solution of $HgSO_4$ in 10% H_2SO_4 was added, and the mixture again allowed to stand in the dark for 60 minutes, after which 20.0 ml of 10% H_2SO_4 and 15 ml of 2 N NaCl were added. Five minutes later 3.0 ml of a saturated solution of KI were added, and the I_2 that separated out was titrated with a solution of $Na_2S_2O_3$. The difference between the overall unsaturation and the percentage of "allyl" double bonds constitutes the percentage of "acrylic'' bonds.

The procedure set forth above was employed for the monomer (allyl acrylate); the results are listed in Table 1.

Procedure for Determining the Molecular Weight of the Polymer

The molecular weight was determined by the cryoscopic method. Benzene was used as the solvent. Solutions containing 2-2.5% of the polymers were used in the determinations.

Table 1

Percentage of "allyl" double bonds	Percentage of "acrylic" double bonds	overall unsaturation
48.2	49.8	98.0
48.3	50.7	99.0
48.2	49.5	97.7

Test Results

We made tests with solutions containing no more than 5.8% by weight of the monomer at the start, as gelatinization was observed to occur at higher concentrations. With the initial concentration of the monomer set at 5.8% a slight amount of the insoluble form of the polymer was observed to form in the final stages of the process (at polymerization depths in excess of 80%). When the initial concentration was kept at 2.5% nothing but soluble polymer was formed throughout the process; that is why we used this concentration for our basic determinations. The initial percentage of benzoyl peroxide was

1% (w/w) of the whole solution for all our tests. The temperature was 60° ± 0.2°.

The data on the percentage of "allyl" and "acrylic" groups in the polymer and on the overall unsaturation of the polymer as functions of the depth of polymerization and the initial concentration of the monomer are given in Tables 2 and 3 and Fig. 2. (We define a polymer with 100% unsaturation as one in which each monomer unit has one side chain with a double bond.)

Table 2

Initial Concentration of Allyl Acrylate ~ 2.5%

Initial percent of allyl acrylate	Initial percent of benzoyl peroxide	Polymerization, per cent	Unsaturation		
			overall	allyl group	Acrylic group
2.72	1.00	19.1	60.0 55.2 } 57.6	58.8	0
2.50	0.96	24.0	56.1 53.8 } 55.0	51.8	3.2
2.52	1.02	34.3	–	49.5 50.5 } 50.0	–
2.47	1.00	39.6	47.8	44.7	3.1
2.56	0.98	41.4	48.8 49.0 } 48.9	46.0	2.9
2.41	0.99	59.2	44.3 44.7 } 44.5	42.2 39.3 } 40.7	3.8
2.36	1.00	70.1	41.7 38.6 37.9 } 39.4	38.0 38.2 } 38.1	1.3
2.56	0.99	78.5	44.0 44.0 } 44.0	37.3 37.0 } 37.1	6.9

Table 3

Initial Concentration of Allyl Acrylate ~ 5.7%

Initial per cent of allyl acrylate	Initial per cent of benzoyl peroxide	Polymerization per cent	Unsaturation		
			overall	allyl group	acrylic group
5.80	1.05	52.9	47.5 46.9 } 47.2	45.3 45.2 } 45.25	2.0
5.56	0.99	76.2	37.9	34.7	3.2
5.70	1.06	86.3	36.5 35.2 } 35.9	–	–

The following conclusions may be drawn from the data of Tables 2 and 3 and Fig. 2.

1. The overwhelming proportion of the polymer's unsaturation is due to the presence of "allyl" bonds in the side chains.

2. As the depth of polymerization increases, both the overall unsaturation and the percentage of "allyl" bonds diminish.

3. The percentage of "acrylic" bonds in the side chains remains negligible (of the order of 3%) throughout the process.

4. Increasing the initial concentration of the monomer causes the overall unsaturation of the polymer and its percentage of "allyl" bonds to drop.

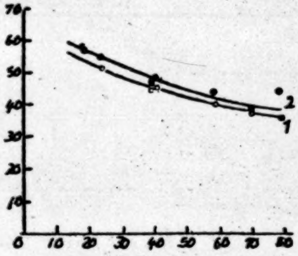

Fig. 2

The data on the determination of the polymer's molecular weight are listed in Table 4.

As the depression observed in our tests was extremely small (0.03-0.05°) , the data listed in Table 4 may serve merely for an approximate evaluation of the magnitude of the molecular weight.

Table 4

Initial percentage of allyl acrylate	Polymerization, per cent	Molecular weight of polymer
5.80	52.9	3100
2.36	70.1	4100
2.56	78.5	2800

Evaluation of Results

The ratio of the "allyl" to the "acrylic" double bonds in the side chains indicates that the main polymer chain is built up chiefly of acrylic bonds of the monomer, i.e., Structure (I) predominates. Structure (II) is present, but in a considerably less degree ($\sim$3% of the entire mass of the polymer).

What has been said above is doubtless true for those parts of the polymer molecules where the double bonds are conserved in the side chains. But, since the overall unsaturation of the polymer (for reasons that will be taken up later) is much less than 100%, there is a certain degree of indeterminacy concerning the structure of the parts of the molecule when there are no double bonds in the side chains.

It may be possible that at the beginning the main chain of the polymer consists not only of "acrylic" double bonds, but has "allyl" bonds as well; the acrylic double bonds are then in the side chains, and then they react owing to the various secondary processes. To test this possibility we undertook to investigate the structure of the polymer in various stages of the process (from 19.1% to 86.3% of polymerization). It was found (Tables 2 and 3) that the percentage of "acrylic" double bonds in the side chains was always negligible, even though the overall unsaturation of the polymer fluctuated quite appreciably.

Thus, it may be considered as established that all the parts of the main chains of the polymer are formed almost exclusively of "acrylic" double bonds, only an extremely small proportion being formed of "allyl" bonds.

The sharp drop in unsaturation during the process (as is evident from Tables 2 and 3 and Fig. 2; this decrease is entirely due to the consumption of the "allyl" double bonds by side chains) indicates that secondary processes of "supplementary polymerization" are taking place. The following two processes seem to us to be the most likely.

1. The "allyl" double bonds in the side chains react with the benzoyl peroxide (or with the free radicals formed during its decomposition) i.e., in other words, an act of initiation occurs in the polymerized molecules formed in the side chains, leading to the growth of new chains. 2. The "allyl" double bonds of the side chains react with the growing chains (free radicals).

In both cases, lattice (three-dimensional) structures arise. When this process of structuralization reaches a certain depth, gelatinization sets in. The considerations set forth above are confirmed by the facts that when the initial concentration of the monomer is increased, the drop in the unsaturation of the polymer is more rapid, and a gel is formed at earlier stages of the polymerization.

The appreciable deviation of the overall unsaturation from 100%, even in early stages of the process, is evidently due to the fact that some peroxide debris enters into the polymer chain during initiation acts and possibly during breaks in the chain; as the molecular weight of the polymer is quite low, this ought to lower the unsaturation appreciably (it should be borne in mind that the molecular weight of 3000-4000 determined by us for the polymer corresponds to a polymer that is already at a considerably advanced stage of structuralization. When the length of the molecular chain is computed for a single initiation act, it obviously is many times smaller). Moreover, it is not impossible that intramolecular cyclization takes place.

The mechanism of formation of the soluble form of the polymer of allyl acrylate described above may be easily conceived of within the framework of the theory of copolymerization. And the facts discovered by us are in agreement with the already studied singular behavior of allyl derivatives when separately polymerized as well as when copolymerized with other unsaturated compounds.

Thus, for example, it is known that when allyl acetate and allyl chloride are polymerized we get polymers with extremely low molecular weights, although the overall velocity of the process is fairly high. This testifies to the fact that acts of initiation occur with marked velocity, while the growth of long chains is rendered more difficult.

In studying the copolymerization of allyl chloride with styrene, it has been shown that the copolymer is strongly enriched with styrene no matter what the composition of the initial mixture [6].

The copolymerization constant for the allyl chloride radical is:

$$\frac{v_{a \cdot a}}{v_{a \cdot s}} = 0.032.$$

The copolymerization constant for the styrene radical is:

$$\frac{v_{s \cdot s}}{v_{s \cdot a}} = 31.3.$$

When the percentage of allyl chloride in the input mixture is increased, the molecular weight of the polymer drops sharply. Thus, the participation of allyl derivatives in the formation of the chain is hampered in this case as well.

In our case, the polymerization of allyl acrylate may be looked upon as a singular copolymerization in which the two components are the "allyl" and "acrylic" bonds of the monomer.

As yet it is hard to state definitely which of the double bonds is responsible for initiation, but it is entirely probable that even in this respect the "allyl" bond is more reactive than the "acrylic" bond. In building up the chain the addition of the monomer units to one another is effected chiefly by the "acrylic" bonds, only about 3% being accounted for by the "allyl" bonds (in the accepted terminology of binary copolymerization, the polymer is considerably enriched in the "acrylic component").

It is worthy of note that if the copolymerization constants found for the allyl chloride-styrene system are used for our experiment, the share of the "allyl addition compound" at the initial moment when the proportion of allyl and acrylic bonds is 1:1 will be:

$$\frac{dA}{dA + dB} = \frac{A\,(\alpha A + B)}{A(\alpha A + B) + B(\beta B + A)} = 0.031, \text{ or } 3.1\%.^{*}$$

The value obtained is quite close to that found by us experimentally. In the course of the process the relative percentage of "allyl" bonds rises, and the proportion of the "allyl addition compound" should be expected to increase somewhat.

Thus, at the very start short polymer molecules are formed, their side chains consisting almost exclusively of "allyl" double bonds. Later on, these bonds enter into initiation acts as well as into acts of growth, at first small highly branched molecules being formed, and later a dense lattice, i.e., gelatinization sets in.

SUMMARY

1. It was established that in the polymerization of allyl acrylate in dilute solutions a product of low molecular weight is formed that is highly

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* The computation was made from the equation for the differential composition of a binary polymer.

soluble in a number of organic solvents.

2. A method was developed for determining the "allyl" and "acrylic" double bonds when they occur together.

3. It has been shown that the principal chain of the polymer of allyl acrylate is formed mainly at the expense of the "acrylic" double bond.

4. It was shown that during the polymerization of allyl acrylate the "allyl" double bonds situated in the side chains of the polymer enter into acts of initiation and growth, resulting in the formation of a lattice structure and, at a certain stage of the process, a gel.

5. The process of polymerization of allyl acrylate is described qualitatively as a singular instance of binary copolymerization. It was shown that the "allyl" double bond exhibits little tendency to enter into chain growth reactions.

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RESEARCH ON THE ALKALOIDS OF HELIOTROPIUM LASIOCARPUM

THE STRUCTURE OF HELIOTRIN

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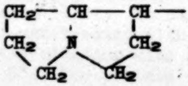
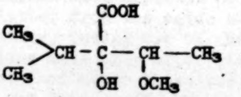
Heliotrin was isolated and studied by one of the present authors even before World War II. Subsequently, the work was interrupted owing to lack of the plant material, and only recently has it been possible to obtain the plant again and conclude the research undertaken. The following data on the chemical nature of this alkaloid were obtained in our prewar research: 1) heliotrin ($C_{16}H_{27}O_5N$) is an ester that decomposes upon alkaline hydrolysis into an unsaturated aminoglycol, $C_8H_{13}O_2N$, called heliotridine, and an acid, $C_8H_{16}O_4$, called heliotrinic acid [1]; 2) The saturated parent substance of heliotridine, which contains no oxygen and is called heliotridane, has the structure of 1-methyl-pyrrolizidine-1 [2], as was later confirmed by Adams [3]; 3) heliotrinic acid has the structure 2-methyl-3-hydroxy-4-methoxypentane-3-carboxylic acid (II) [4]; 4) When heliotrin is catalytically reduced with platinum, it absorbs 2 molecules of hydrogen, the heliotridine's double bond and esterified hydroxyl group being restored; the products of reaction are an amino alcohol, $C_8H_{15}ON$, called hydroxyheliotridane, and free heliotrinic acid [5]. As may be seen from this brief review, the structure of heliotrinic acid and of heliotridane, the parent substance of the aminoglycol, was already established by us, and, since this aminoglycol and heliotrinic acid are the sole products of the hydrolysis of heliotrin, the only things remaining to be cleared up to establish the structure of the latter were the position of the two hydroxyl groups and of the double bond in the amino glycol. The elucidation of this problem is the subject of the present paper.

First of all, we decided to clear up the position of the heliotridine hydroxyl group that is not reduced upon catalytic reduction. To do this the amino alcohol, hydroxyheliotridane, that is formed in the catalytic reduction of heliotrin was oxidized with chromic acid under the conditions employed by Willstatter to oxidize tropine to tropinone. Though in our case the reaction was by no means as smooth as in the case of tropine, we were nevertheless able to obtain an amino ketone, with the formula $C_8H_{13}ON$, in a yield that was about 23% of the theoretical, based on the hydroxyheliotridane entering into the reaction. This comparatively low yield of the amino ketone is due to the fact that it breaks down easily upon oxidation; that is why a large part of the amino alcohol is recovered when the chromic acid is employed in the amounts required to oxidize the hydroxyl group of the amino alcohol, the oxidant being consumed in the further oxidation of the amino ketone. The constants of the amino ketone synthesized by us coincide precisely with the constants of retronecanone [7] synthesized by Adams as the result of oxidizing retronecanol with cyclohexanone. For a direct comparison, we prepared retronecanol by catalytic reduction of the alkaloid seneciphylline [8] and oxidized the retronecanol with chromic acid under the conditions we used for oxidizing the hydroxyheliotridane. The direct comparison of the amino ketone thus synthesized with the amino ketone prepared from the hydroxyheliotridane established that they were identical. The identity of these amino ketones indicates that the amino alcohols from which they were synthesized have the same structure, the difference between them being due to stereoisomerism. Adams established the following structure for retronecanol: 1-methyl-6-hydroxypyrrolizidine (III) [9]. It is evident that hydroxyheliotridane must have the same structure. This fact sheds new light upon the structure of heliotridine, pointing to an analogous structure for this amino glycol and retronecine, for which Adams established Structure (IV) [9]. And if we remember that the esters of retronecine undergo the same changes under catalytic reduction as the esters of heliotridine, i.e., that in this case the double bond and one of the hydroxyl groups of the amino glycol are reduced, as was established by Barger [10], the assumption concerning the identical structure of the two amino glycols becomes self-evident. With this assumption in mind, as the result of the elimination of the heliotridine's double bond and secondary hydroxyl group, there was reason to believe we could synthesize the saturated amino alcohol, isoretronecanol, which Adams synthesized by eliminating these retronecine groups and for which he established the structure (IX) [7].

The endeavor to synthesize isoretronecanol from heliotridine seemed to us to be all the more interesting in that the asymmetrical carbon atoms of isoretronecanol are not bound to a hydroxyl group. And since heliotridine and retronecine are derivatives of the same l-heliotridane, isoretronecanol and the amino alcohol of heliotridine (if the latter could be synthesized) could not differ in steric configuration, and the identity of their structures could be resolved by direct comparison. Therefore, in order to eliminate the secondary hydroxyl group and the double bond of heliotridine we performed a series of subsequent reactions, which actually resulted in the synthesis of isoretronecanol. As the synthesis of isoretronecanol was established not only by the structure of the end product, but also by that of all the intermediate products, we felt it was necessary, in describing the reactions that took us from heliotridine to isoretronecanol, to cite the structure of the intermediates for the sake of clarity. The heliotridine was reduced with Rainey's nickel; this mainly reduced the double bond, resulting in the saturated amino glycol that we have named dihydroxyheliotridane (V). Benzoylation of the dihydroxyheliotridane by benzoyl chloride, 0.5 mole of which was taken per mole of the amino glycol, resulted in the formation of the ester — monobenzoyl-dihydroxyheliotridane (VI). When thionyl chloride acted upon the latter, the reaction was twofold: substitution of chlorine for the hydroxyl group occurred to a negligible degree; the principal reaction being the splitting off of water and the formation of the benzoate of the unsaturated amino alcohol (VII). The latter was also reduced and saponified catalytically. When the synthesized amino alcohol (IX) and its benzoate (VIII) were compared directly with the isoretronecanol and its benzoate, prepared from plainecine by Adams' method [7], they were found to be absolutely identical. This proved that the second hydroxyl group of heliotridine that was esterified by heliotrinic acid occupies the same position in the system of 1-methylpyrrolizidine as the corresponding hydroxyl group of retronecine. Thus, all we still needed for the structure of heliotridine was elucidation of the position of the double bond. Our discovery and investigation of the new alkaloid supinin greatly facilitated the clarification of this problem. Upon hydrolytic decomposition, this alkaloid forms trachelanthinic acid and an unsaturated amino alcohol, $C_8H_{13}ON$, which was given the name of supinidine. We were able to prove that supinidine is a derivative of l-heliotridane and has the structure (X) [11]. As this formula indicates, the supinidine double bond is in the same position as the double bond of retronecine (IV). Therefore, if our assumptions that heliotridine and retronecine are diastereoisomers are correct, supinidine ought to be synthesized by the elimination of the secondary hydroxyl group in heliotridine. This elimination was effected as a result of the following reactions. Heliotrine was subjected to the action of thionyl chloride, and the reaction product was reduced, without purification, by chromium chloride ($CrCl_2$) in the presence of zinc. This resulted in a noncrystallizing oily product, which yielded heliotrinic acid and a saturated amino alcohol after saponification. When this amino alcohol was directly compared with supinidine, both as bases and in the form of their respective picrates and iodomethylates, they were found to be identical. It is easy to see that the production of supinidine from heliotridine not only clears up the last problem involved in the structure of heliotridine, namely, the position of the double bond, but again confirms the primary nature of the reducible hydroxyl group of this amino glycol. Thus it must be considered demonstrated that heliotridine has the same structure as retronecine (IV), the difference between them being due to the different steric configuration of the asymmetric nucleus at position 6 of the pyrrolizidine ring. It follows therefore, if we bear in mind the structure of heliotrinic acid (II), already proved by us, that the structure of heliotrine is expressed by formula (XI).



(I)



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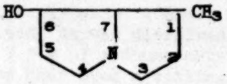

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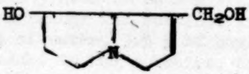

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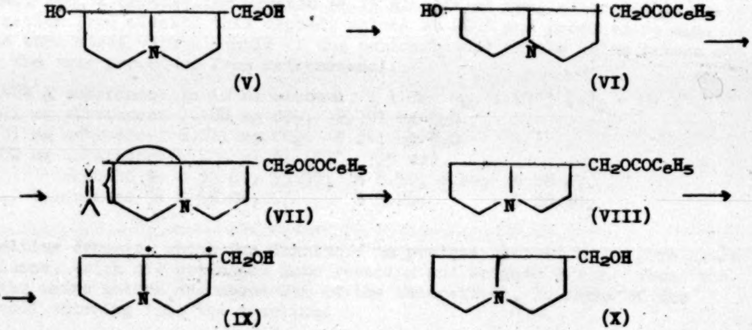

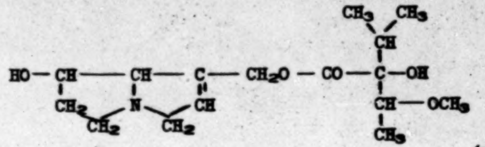

(XI)

EXPERIMENTAL

Oxidation of Hydroxyheliotridane

15 g of hydroxyheliotridane were dissolved in 300 ml of glacial acetic acid, and 7.25 g of chromic anhydride dissolved in a mixture of 7 ml of water and 70 ml of glacial acetic acid were added, with mechanical stirring, to the solution at 60-70° over the space of one hour. After all the chromic anhydride had been added, the solution was heated to 60-70° over a water bath until all the chromic acid had been reduced, then chilled with ice, and finally extracted with ether after it had been alkalinized with a 40% solution of caustic potash. The ether extract was dried with potash, and the ether then driven off. There remained about 14 g of a yellow oil, which crystallized when crystals of hydroxyheliotridane were placed in it. To separate the latter from the amino ketone, the crystallized mass was treated with boiling pentane, (using two batches of 50 ml each), the latter blending with the crystalline mass only after standing for 10-15 minutes at 0°. The pentane solutions obtained after these two extractions were combined together, and the solvent was driven off. There remained about 4 g of an uncrystallizable mobile oil, which proved to be a mixture of the amino ketone and hydroxyheliotridane. The semicarbazone was obtained from this mixture. To this end, it was dissolved in 50 ml of water, 3.5 g of semicarbazide hydrochloride and 7.5 g of sodium acetate were added to the solution, and the whole heated for an hour over a boiling water bath. The cooled solution was filtered to remove the slight amount of sludge and alkalinized with a solution of caustic soda to a pH of 10-11. When it was allowed to stand and then rubbed with a small rod, a crystalline deposit (1.75 g) settled out; after double recrystallization from alcohol this deposit melted at 209° and produced no m.p. depression when mixed with a sample of the semicarbazone of the amino ketone obtained by the same procedure from retronecanol.

0.1424 g substance: in 10 ml alcohol; l 1 dm; α_D -1.27°; $[\alpha]_D$ - 89.1°.
3.671 mg substance: 7.488 mg CO_2; 2.791 mg H_2O.
2.951 mg substance: 6.011 mg CO_2; 2.241 mg H_2O.
2.780 mg substance: 0.724 ml N_2 (27°, 735 mm).

	C	H	N
Found %:	55.63, 55.55;	8.50, 8.49;	28.67.
$C_9H_{16}ON_4$. Calculated %:	55.04;	8.26;	28.55.

The crystalline deposit, which was insoluble in pentane, proved to be pure hydroxyheliotridane, which did not enter into reaction and weighed 9.5 g. Thus, the yield of the amino ketone was about 23% of the theoretical, in terms of the amino alcohol entering into the reaction.

Oxime of the amino ketone. 0.6 g of the semicarbazone was dissolved in 12 ml of a 1 N solution of hydrochloric acid, and the solution produced was heated over a boiling water bath for 30 minutes. The cooled solution was then treated with an excess of a 40% solution of caustic soda and immediately extracted with ether. After the ether solution had been dried and the ether driven off, there remained behind a mobile oil, from which the oxime was prepared. This was effected by adding to the oil 4.8 ml of a 10% solution of caustic soda and 0.8 g of hydroxylamine hydrochloride, and heating the whole for 20 minutes over a boiling water bath. The cooled solution was acidulated with hydrochloric acid to a pH of 8.5 and extracted with ether. The ether solution was dried with sodium sulfate, and the ether then driven off. This yielded 0.3 g of a crystalline product, which was first sublimed in vacuum (100°, 2 mm) to purify it and then recrystallized from ether. After that the substance consisted of white needles that melted at 165-167°. A mixed sample with the oxime of the amino ketone prepared from retronecanol fused at the same temperature.

0.0807 g substance: in 10 ml alcohol; 1 1 dm; α_D −0.62°; $[\alpha]_D$ −76.8°.
3.210 mg substance: 0.521 ml N_2 (21°, 733 mm).
3.046 mg substance: 0.490 ml N_2 (21°, 733 mm).
Found %: N 18.16, 18.00.
$C_8H_{14}ON_2$. Calculated %: N 18.18.

Picrate of the amino ketone. This salt is precipitated when alcoholic solutions of the base and of picric acid are mixed together. After recrystallization from alcohol the picrate was obtained as yellow needles that melted with decomposition at 195°.

A mixed sample with the picrate of the amino ketone prepared from retronecanol fused at the same temperature.

2.282 mg substance: 0.313 ml N_2 (23°, 740 mm).
Found %: N 15.40.
$C_8H_{13}O_2N \cdot C_6H_3O_7N_3$. Calculated %: N 15.21.

Reduction of Heliotridine With Rainey's Nickel —

Preparation of Dihydroxyheliotridane

7.5 g of heliotridine were dissolved in 40 ml of ethyl alcohol. To the solution there was added 2.5 g of the catalyst, and the whole was shaken up under slight excess pressure in an atmosphere of hydrogen. During 2.5 hours 1.100 ml of hydrogen was absorbed, and the absorption stopped. The catalyst was filtered out of the solution, and crystalline picric acid crushed to a powder was added, while the solution was heated, until the latter gave an acid reaction with methyl orange. After cooling a large amount of the picrate (15 g) settled out; after recrystallization from alcohol this picrate, in the form of yellow needles, melted at 157-158°.

3.904 mg substance: 0.512 ml N_2 (26°, 736 mm).
Found %: N 14.60.
$C_8H_{25}O_2N \cdot C_6H_3O_7N_3$. Calculated %: N 14.51.

To obtain the free base, 15 g of the picrate, crushed to a fine powder, was treated with 60 ml of a 1 N solution of hydrochloric acid. All the picric acid was extracted with ether. The remaining acid solution was alkalinized with a solution of caustic soda to a pH of 11, and the water was driven off in vacuum. The dry residue was extracted with absolute alcohol. After the alcohol had been driven off there remained an oily residue (6 g), which crystallized only after prolonged standing over calcium chloride in vacuum. The base was recrystallized from acetone, after which its white prisms had a m.p. of 76-77°.

0.3357 g substance: in 10 ml absolute alcohol; $\underline{l}$ 1 dm; α_D-1.14°; $[\alpha]_D$-34°.
3.995 mg substance: 8.950 mg CO_2; 3.471 mg H_2O.
3.877 mg substance: 8.668 mg CO_2; 3.268 mg H_2O.
5.644 mg substance: 0.452 ml N_2; (24°, 733 mm).
5.578 mg substance: 0.449 ml N_2; (22°, 739 mm).
Found %: C 61.09, 60.98; H 9.72, 9.43; N 8.87, 9.06.
$C_8H_{15}O_2N$. Calculated %: C 61.10; H 9.61; N 8.91.

Dihydroxyheliotridane dissolves easily in water and alcohol, is less soluble in acetone, and is rather poorly soluble in chloroform and ether.

Monobenzoyldihydroxyheliotridane

5.8 g of dihydroxyheliotridane was dissolved in 300 ml of anhydrous chloroform, and a solution of 2.6 g of benzoyl chloride (0.5 mole) in 20 ml of chloroform was added to the solution drop by drop with vigorous shaking. As this went on, the solution grew cloudy, and oily drops, consisting mainly of dihydroxyheliotridane hydrochloride, were observed to separate out. After all the benzoyl chloride had been added, the reaction mass was boiled for 2 hours with a reflux condenser. This resulted in the separation of some more of the oily deposit. All the chloroform was then driven off. To eliminate acid impurities, the residue was dissolved in a 5% solution of hydrochloric acid and extracted with ether. When this acid solution was alkalinized with a strong solution of ammonia, an oil separated out; this oil was taken up with chloroform. The water was removed from the chloroform solution with sodium sulfate, and the chloroform then driven off. What remained was an oily substance that did not crystallize upon prolonged standing. It was assumed that this substance was contaminated with a small amount of dihydroxyheliotridane, which, though not extracted from aqueous solutions by chloroform, might well be here extracted by monobenzoyldihydroxyheliotridane. Hence, to purify the product obtained of its dihydroxyheliotridane, it was again dissolved in hydrochloric acid and precipitated from the acid solution by ammonia. The oil that settled out crystallized only after prolonged rubbing with a rod under a water layer. The crystalline mass was drawn off, washed with water, and, after drying in vacuum over calcium chloride, recrystallized from acetone.

We obtained 3 g of white acicular crystals, which melted at 133-134°.

2.344 g substance: in 10 ml chloroform; $\underline{l}$ 1 dm; α_D -1.19°. $[\alpha]_D$ -5.08°.
3.508 mg substance: 8.890 mg CO_2; 2.300 mg H_2O.
3.877 mg substance: 9.346 mg CO_2; 2.491 mg H_2O.
7.356 mg substance: 0.361 ml N_2 (25°, 734 mm).
7.814 mg substance: 0.385 ml N_2 (27°, 738 mm).
Found %: C 69.11, 69.24; H 7.34, 7.19; N 5.43, 5.43.
$C_{15}H_{19}O_3N$. Calculated %: C 68.94; H 7.34; N 5.36.

Monobenzoyldihydroxyheliotridane is poorly soluble in water, but is soluble in alcohol and chloroform.

The ammoniacal mother liquors from which the monobenzoyldihydroxyheliotridane was separated, were combined and alkalinized with a 20% solution of caustic soda until it gave an alkaline reaction with tropaeolin O, after which the water and ammonia were driven off in vacuum. The dry residue was then treated as described above in the preparation of dihydroxyheliotridane. This yielded 2.3 g of dihydroxyheliotridane that had not entered into the reaction.

Monobenzoyldihydroxyheliotridane picrate. This salt was prepared by adding an alcoholic solution of picric acid that had been saturated in the cold to an alcoholic solution of the base. After recrystallization from alcohol the picrate had the form of beautifyl yellow needles that melted at 95°. The picrate evidently settles out of alcohol together with the crystallization solvent, since its melting point rises to 134-135° after it is dried at 80° to constant weight. The dried salt was used in analysis.

3.896 mg substance: 0.395 ml N_2 (25°, 735 mm).
2.858 mg substance: 0.289 ml N_2 (24°, 735 mm).
Found %: N 11.22, 11.25.
$C_{15}H_{19}O_3N \cdot C_6H_3O_7N_3$. Calculated %: N 11.42.

Reaction of Monobenzoyldihydroxyheliotridane With Thionyl Chloride

To 2.5 g of monobenzoyldihydroxyheliotridane, rubbed to a fine powder, there was added drop by drop while chilled with ice 5 g of thionyl chloride that had been purified with quinoline and cottonseed oil. When all the thionyl chloride had been used up, the reaction mass was set aside to stand at room temperature for an hour, after which it was heated for an hour with a reflux condenser over a boiling water bath. The excess thionyl chloride was driven off in vacuum, and the noncrystallizing residue was dissolved in a small amount of chloroform. When anhydrous ether was added to the chloroform solution, a mixture of the hydrochlorides settled out as a crystalline precipitate. This mixture was separated as follows. The precipitate was dissolved with heating in ten times its volume of acetone. When the solution had cooled to room temperature, a crystalline precipitate settled out; this was drawn off and washed with an extremely small quantity of acetone (hydrochloride A).

The acetone mother liquor was reduced to about one fifth its volume and set aside to stand at room temperature; a crystalline deposit slowly settled out (hydrochloride B). After this precipitate had been filtered out and washed with a small amount of acetone, the mother liquor and the wash acetone were combined, and anhydrous ether was added; this resulted in the precipitation of a third crystalline deposit (hydrochloride C).

Hydrochloride A was dissolved in a small amount of water, then alkalinized with a strong solution of ammonia and extracted with ether. After the ether solution had been dried with sodium sulfate and the ether driven off there remained an oil, part of which crystallized when a tiny crystal of monobenzoyldihydroxyheliotridane was placed in it. The crystals were drawn off from the oil, washed with a small amount of acetone, and recrystallized from acetone. Direct comparison established their identity with monobenzoyldihydroxyheliotridane. The oil from which the crystals had been separated and the wash acetone were combined, and the acetone driven off. The residue was dissolved in a small quantity of alcohol. An alcoholic solution of picric acid was added to the solution. The precipitate that settled out was the picrate, which was repeatedly recrystallized from alcohol until it had the constant m.p. of 146-147°.

Hydrochloride B was dissolved in a small quantity of water. The aqueous solution was alkalinized with a strong solution of ammonia and then extracted with ether. After the ether solution had been dried with sodium sulfate and the ether driven off there remained a noncrystallizing oil, from which the picrate was obtained in an alcoholic solution. After several recrystallizations from alcohol this picrate likewise melted at 146-147°. The salt contains no halides.

4.564 mg substance: 0.487 ml N_2 (24°, 731 mm).
Found %: N 11.82.
$C_{15}H_{17}O_2N \cdot C_6H_3O_7N_3$. Calculated %: N 11.88.

A free base that did not crystallize upon standing was also obtained from hydrochloride C. From this base in an alcoholic solution we obtained the picrate, which melted at 162-163° after repeated recyrstallization from a large quantity of alcohol. To judge by its chlorine content, it is the picrate of monobenzoyldihydroxyheliotridane in which a hydroxyl group has been replaced by chlorine.

5.570 mg substance: 1.610 mg AgCl (Carius).
5.420 mg substance· 1.535 mg AgCl (Carius).
Found %: Cl 7.15, 7.00.
$C_{15}H_{18}O_2NCl \cdot C_6H_3O_7N_3$. Calculated %: Cl 6.97.

The Hydrochloride of the Base, Isolated From the Picrate with a M.P. of 146-147°

The picrates with a m.p. of 146-147° prepared from hydrochlorides A and B were combined (total weight about 1.7 g) and treated with 30 ml of 1 N solution of hydrochloric acid. The mixture was extracted with ether until all the picric acid had entered the ether and the aqueous solution was completely colorless. Then the acid solution was alkalinized with a strong solution of ammonia and extracted with ether. The ether solution was dried with sodium sulfate, and the ether driven off. There remained an oil that did not crystallize upon standing. From this oil we obtained the hydrochloride. To do this, we dissolved the base in a small quantity of absolute alcohol and added an alcoholic solution of hydrochloric acid to the solution. After absolute ether was added to the alcoholic solution a crystalline deposit precipitated out; this deposit was then recrystallized from anhydrous acetone.

We obtained 0.7 g of colorless crystals that melted at 147-148°. To judge from the results of analysis, this substance is the benzoic hydrochloride of the unsaturated amino alcohol.

0.1812 g substance: in 10 ml alcohol; $\underline{1}$ 1 dm; $\alpha_D - 1.66°$;
$[\alpha]_D - 91.7°$.
3.556 mg substance: 8.430 mg CO_2; 1.990 mg H_2O.
3.523 mg substance: 8.330 mg CO_2; 1.959 mg H_2O.
7.988 mg substance: 0.363 ml N_2 (27°, 725 mm).
7.770 mg substance: 0.382 ml N_2 (28°, 721 mm).
5.385 mg substance: 2.800 mg AgCl (Carius).
5.105 mg substance: 2.585 mg AgCl (Carius).
Found %: C 64.65, 64.46; H 6.26, 6.22;
N 4.93, 5.28; Cl 12.86, 12.53.
$C_{15}H_{17}O_2N \cdot HCl$. Calculated %: C 64.37; H 6.49; N 5.01; Cl 12.67.

Reduction of the Benzoate of the Unsaturated Amino Alcohol With a Platinum Catalyst – Preparation of Isoretronecanol

0.65 g of the hydrochloride was dissolved in 10 ml of absolute alcohol; to the solution there was added a catalyst (0.3 g of H_2PtCl_6), and the whole was agitated in a hydrogen atmosphere with slight excess pressure. About 1 mole of hydrogen was soon absorbed, and the absorption stopped. The catalyst was filtered out of the solution, and the alcohol was driven off in vacuum. The residue crystallized completely after cooling. The crystalline mass was recrystallized from anhydrous actone. This yielded tiny needles with a m p. of 180-181°.

0.[illegible]04 g substance: in 10 ml absolute alcohol; $\underline{l}$ 1 dm; α_D – 1.44°; $[\alpha]_D$ – 49.6°.

3.898 mg substance: 9.080 mg CO_2; 2.531 mg H_2O.
3.246 mg substance: 7.552 mg CO_2; 2.100 mg H_2O.
7.596 mg substance: 0.358 ml N_2 (27°, 727 mm).
5.385 mg substance: 0.244 ml N_2 (24°, 733 mm).
Found %: C 63.53, 63.45; H 7.26, 7.24; N 5.12, 5.03.
$C_{15}H_{19}O_2N \cdot HCl$. Calculated %: C 63.91; H 7.16; N 4.97.

A mixed sample of this hydrochloride and the hydrochloride of benzoylisoretronecanol (m.p. 180-181°) prepared by Adams' method from platinecine caused no depression of the melting point. A base was prepared from the hydrochloride in the usual manner, and from the base a picrate, which melted at 130-131° after recrystallization and caused no depression of the melting point when mixed in a test sample with benzoylisoretronecanol picrate. For further confirmation that the substance we had synthesized was the benzoate of isoretronecanol, we saponified it. The amino alcohol thus formed was used in preparing the picrate and iodomethylate, which were compared directly with the same salts of isoretronecanol. This comparison proved them to be fully identical.

Reaction of Heliotrin With Thionyl Chloride

15 g of thionyl chloride, purified with quinoline and cottonseed oil, was added drop by drop, with ice-chilling, to 6 g of the alkaloid, ground to a fine powder. After the thionyl chloride had been added, the reaction mass was set aside to stand for one hour at room temperature, and then heated for 1.5 hours with a reflux condenser over a boiling water bath. The excess thionyl chloride was driven off in vacuum, leaving behind an oily reaction product, which was dissolved in 50 ml of a 3% solution of hydrochloric acid. The acid solution produced was purified by shaking it up with activated charcoal, the charcoal was filtered out, and about 20 ml of water was driven out of the solution in vacuum to free it from sulfuric acid. In this state the solution was used in reduction.

Reduction of the Product of the Reaction Between Heliotrine and Thionyl Chloride

75 g of $CrCl_3 \cdot 6H_2O$, 225 ml of concentrated hydrochloric acid, and 75 g of amalgamated granulated zinc were placed in a two-necked flask fitted with a reflux condenser and a dropping funnel. The free end of the condenser was closed by a hydraulic lock. The reaction mixture was heated to 130-140° over an oil bath until the color of the solution changed from green to light blue. In this process some unreacted zinc was left over. To the reducing mixture thus produced

there was added through the dropping funnel an acid solution of the product of the reaction between heliotrine and thionyl chloride (vide supra). The chromium was observed to oxidize rapidly, and the solution turned green. The reaction mixture was then heated over an oil bath until the solution turned light blue again, after which it was cooled and treated with a strong solution of ammonia. The inorganic precipitate was filtered out and washed several times with hot water until all the organic bases had been leached out. The filtrate and the wash waters were combined and extracted with chloroform The chloroform extract was leached out twice with a small quantity of a 10% solution of sulfuric acid. The acid solution was treated with an excess of strong ammonia solution and exhaustively extracted with ether. The ether solution was dried with sodium sulfate, and the ether driven off. There remained about 3 g of a noncrystallizing oily product. In order to saponify this product it was dissolved in 25 ml of alcohol, 25 ml of a 10% solution of caustic soda was added to the solution, and the whole was heated for 1.5 hours with a reflux condenser over a boiling water bath. The alcohol was driven out of the solution, and a current of live steam was passed through the remaining alkaline aqueous solution; this caused the volatile bases to pass off with the steam.

Steam distillation was continued until the distillate no longer gave a reaction with silicotungstic acid. After the volatile bases had been driven off, the alkaline solution was cooled and extracted with ether. The ether solution was dried with potash, and the ether driven off. The residue was distilled in vacuum The yield was about 1 g of a thick, noncrystallizing oil that distilled over at 118° (2 mm). From an alcoholic solution of this substance we prepared the picrate, which was obtained as yellow needles that melted at 142-143° after recrystallization from alcohol.

3.494 mg substance: 0.474 ml N_2 (20°, 733 mm).
3.287 mg substance: 0.443 ml N_2 (20°, 733 mm).
Found %: N 15.25, 15.15.
$C_8H_{13}ON \cdot C_6H_3O_7N_3$. Calculated %: N 15.22.

A mixed sample of this picrate with the picrate of supinidine (m.p. 142-143°) caused no depression of the melting point. We prepared the free base from this picrate by the method described in the preceding experiments and determined its specific rotatory power:

0.1094 g substance: in 1 ml of alcohol; $\underline{1}$ 0.5 dm; α_D -0.55°; $[\alpha]_D$ - 10.06°.

This specific rotatory power coincides with the specific rotatory power of supinidine (-9.45°) within the limits of experimental error. From the base we prepared the iodomethylate. This was done by dissolving it in ether and adding methyl iodide to the solution. When the solution was set aside to stand, crystals of the iodomethylate separated out; after reprecipitation by anhydrous ether from anhydrous methanol the iodomethylate was in the form of beautiful snow-white needles with a m.p. of 112-113°.

0.1150 g substance: in 1 ml methanol; $\underline{1}$ 0.5 dm; α_D -0.58°; $[\alpha]_D$ -10.09°.
9.910 mg substance: 3.51 ml 0.01 N solution H_2SO_4 (Kjeldahl).
10.266 mg substance: 3.51 ml 0.01 N solution $H2SO_4$ (Kheldahl).
0.1025 g substance: 36.4 ml 0.01 N $AgNO_3$ solution.
Found %: N 4.96, 4.78; I 45.07.
$C_8H_{13}ON \cdot CH_3I$. Calculated %: N 4.98; I 45.14.

All the constants of this iodomethylate coincided precisely with the constants of supinidine iodomethylate, which was prepared by exactly the same method for purposes of comparison. A mixed test sample of the two iodomethylates caused no depression of the melting point.

The alkaline solution from which the amino alcohol that proved to be identical with supinidine was extracted with ether was acidulated with a 20% solution of hydrochloric acid against Congo indicator and then extracted with chloroform. The chloroform solution was dried with sodium sulfate, and the chloroform driven off. The crystallizing residue was recrystallized from a mixture of two parts of benzene and eight parts of petroleum ether. This yielded about 1.1 g of a substance that was identical with heliotrinic acid.

The water distillate with which the volatile bases had been driven off was treated with a large quantity of 40% caustic soda solution and then extracted with ether. The ether solution was dried with potash, and the ether driven off. The residue (0.5 g) was distilled under ordinary pressure. The substance distilled over at 160-170°. The fact that the melting point of the picrate prepared from this substance was not sharp, and that it greedily reduced permanganate in dilute sulfuric acid led us to assume that this substance is a mixture containing an unsaturated base. To determine whether the 1-methyl pyrrolizidine ring existed in these bases, the mixture was reduced with a platinum catalyst. This yielded a base identical with _l_-heliotridane.

SUMMARY

1. After our prewar research on heliotrin, the only problem still unclear concerning its structure was the position of two hydroxyl groups and of the double bond of heliotridine, an amino glycol formed when the alkaloid is hydrolyzed.

2. Oxidation of hydroxyheliotridane ($C_8H_{15}ON$), an amino alcohol produced by the catalytic reduction of heliotrine, yielded an amino ketone, $C_8H_{13}ON$, identical with retronecanol. As the structure of the latter is 1-methyl-6-ketopyrrolizidine, dihydroxyheliotridane and the amino alcohol corresponding to this ketone must have Structure (III). This established the position of the hydroxyl group in heliotridine that resists reduction.

3. Elimination of this secondary hydroxyl group and of the double bond of heliotridine resulted in the formation of an amino alcohol that was identical with isoretronecanol, which is known to have Structure (IX). This demonstrated the position of the second hydroxyl group in heliotridine that does not resist reduction.

4. Elimination of heliotridine's secondary hydroxyl group alone (leaving the double bond untouched) yielded an unsaturated amino alcohol, supinidine, the structure of which was already known to us (X). It follows that heliotridine's double bond must lie between the first and second carbon atoms of the pyrrolizidine ring.

5. It follows from all the foregoing that heliotridine must possess Structure (IV), whereas heliotrin itself (in view of the previously proved structure of heliotrinic acid) must have Structure (XI).

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THE CATALYTIC ACID-FREE ESTERIFICATION OF BENZYL ALCOHOL

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The literature contains numerous investigations devoted to the acid-free esterification of aliphatic alcohols by catalysis, but there is no report of any research on the esterification of the aromatic alcohols. We investigated the acid-free esterification of benzyl alcohol over a copper-zirconium catalyst; it was found that when benzyl alcohol is passed over a freshly prepared and deposited copper-zirconium catalyst at 225° a condensate is formed that contains up to 42% of benzaldehyde, 10.2% of benzyl benzoate, and small amounts of benzoic acid (1.76%) and toluene (0.38%).

As toluene is formed by reduction of the benzaldehyde, we proposed to eliminate this process by passing the vapors of benzyl alcohol over the catalyst together with air or oxygen; it was found that in the presence of air the composition of the condensate differs only slightly from that obtained when pure benzyl alcohol is passed over the catalyst.

Carrying out the process in an atmosphere of oxygen, we observed a sharp drop in the amount of the ester in the condensate, together with the formation of a large amount of benzaldehyde, as high as 57%. In all our tests the amount of toluene produced did not exceed 0.5%. It is of some interest to note that when benzyl and ethyl alcohols are passed over the copper-zirconium catalyst together in a 1:1 mixture at 225°, up to 9% of the ester is formed, together with 43.5% of aldehydes and a small amount of acids (1%), with no noticeable formation of toluene. Thus, when benzyl alcohol is passed over a copper-zirconium catalyst, it behaves like an aliphatic alcohol, forming an ester, an aldehyde, an acid, and – differing from these other alcohols – a small amount of toluene.

EXPERIMENTAL

The copper-zirconium catalyst was prepared by the method suggested by M.M. Koton [1]. The tests were run in standard apparatus. The amount of catalyst in the tube was 40.0 g. The feed rate of the benzyl alcohol was 15 ml/hour. The rate of gas supply was 1 liter/hour. Temperature was 225°. The condensate was analyzed in the usual manner [2].

The results of the tests are listed in the table below.

Test No.	Mixture passed through	Quantity		Analysis of condensate, %			
		Alcohol, ml	condensate, ml	Acid	Ester	Aldehyde	Toluene
1	Pure benzyl alcohol	30	29	1.76	10.18	42.43	0.38
2	Benzyl alcohol + air	30	28	0.67	9.49	45.05	0.56
3.	Benzyl alcohol + + oxygen	30	29	1.95	3.81	56.98	0.46
4	Benzyl alcohol + ethyl alcohol(1:1)	20	19	1.12	9.0	43.49	-

SUMMARY

1. It was proved that when benzyl alcohol is passed over a copper-zirconium catalyst, the condensate formed contains up to 42% of benzaldehyde and up to 10% of benzyl benzoate, together with small amounts of benzoic acid and toluene.

2. When benzyl alcohol is passed over a copper-zirconium catalyst in the presence of oxygen, the condensate contains up to 56% of benzaldehyde.

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SYNTHESIS OF 1,5-DIPHENYLPENTYNE-1-OL-3 AND ITS DERIVATIVES

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It has been established from our experimental data [1,2] and the data of other authors [3,4,5] that independent of their structure, secondary and tertiary acetylenic alcohols and acetylenic esters do not undergo spontaneous polymerization upon long standing (8 to 13 months). Ethylenic-acetylenic alcohols [6] and esters [6], however, polymerize upon standing, no matter what the position and varying structure of their hydrocarbon radicals, forming polymers of various types.

In our present research, we effected a Grignard synthesis of the secondary acetylenic alcohol 1,5-diphenylpentyne-1-ol-3 to confirm this,

$$C_6H_5 - C \equiv C - CHOH - CH_2 - CH_2 - C_6H_5$$

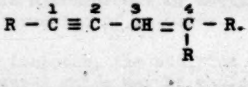
and its acetic ester

$$C_6H_5 - C \equiv C - CHOCOCH_3 - CH_2 - CH_2 - C_6H_5$$

from phenylacetylene and hydrocinnamic aldehyde.

The acetylenic alcohol and ester underwent no visible change in 10 months. They were light-yellow, viscous liquids that dissolved with ease in ethyl alcohol, ether, benzene, and chloroform.

We have already reported [1,2] that methyl and iso radicals in positions 3 and 4 are responsible for the instability of ethylenic-acetylenic hydrocarbons, and that the latter polymerize spontaneously.



$$R - \overset{1}{C} \equiv \overset{2}{C} - \overset{3}{CH} = \underset{R}{\overset{4}{C}} - R.$$

A normal chain structure, consisting of two or more carbon atoms at position 4, stabilizes them even if there are methyl or iso radicals at positions 1, 3, and 4; the latter then have no effect upon the polymerization process. Ethylenic-acetylenic hydrocarbons possessing this structure are stable compounds.

Dehydration of 1,5-diphenylpentyne-1-ol-3 by phosphoric anhydride resulted in the ethylenic-acetylenic hydrocarbon 1,5-diphenylpenten-3-yne-1,

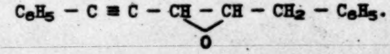
$$C_6H_5 - C \equiv C - CH = CH - CH_2 - C_6H_5,$$

which likewise proved to be a stable compound, as it suffered no visible change when kept in a paraffin coated test tube for 8 months.

Thus, the benzyl radical attached to carbon atom 4 stabilizes an ethylenic-acetylenic hydrocarbon just as hydrocarbon radicals of normal structure, consisting of two or more carbon atoms.

The ethylenic acetylenic hydrocarbon 1,5-diphenylpenten-3-yne-1 was oxidized by acetyl hydroperoxide.

This yielded an oxide of the hydrocarbon



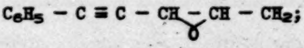
$$C_6H_5 - C \equiv C - \underbrace{CH - CH}_{O} - CH_2 - C_6H_5.$$

The existence of a triple bond in the oxide was demonstrated by bromination; it was found that only two atoms of bromine are added to the oxide, as seen in Table 1, instead of the expected four bromine atoms.

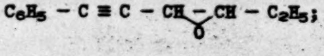
TABLE 1

Quantity of oxide (g)	Amount of bromine (g) required for addition		Actually added
	to the triple bond	to the double bond	
0.9478	1.2961	0.6481	0.6521

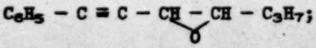
When oxides possessing different structures [1] were oxidized:



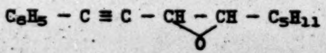
$$C_6H_5 - C \equiv C - \underbrace{CH - CH}_{O} - CH_2;$$



$$C_6H_5 - C \equiv C - \underbrace{CH - CH}_{O} - C_2H_5;$$



$$C_6H_5 - C \equiv C - \underbrace{CH - CH}_{O} - C_3H_7;$$



$$C_6H_5 - C \equiv C - \underbrace{CH - CH}_{O} - C_5H_{11}$$

four bromine atoms were added to the triple bond. This enabled us to establish the presence of the acetylenic bond in oxides and to assume that the oxidation of ethylenic-acetylenic hydrocarbons by acetylhydroperoxide takes place at the double bond with the formation of an oxide.

In the present instance, the addition of only two bromine atoms to the 1,5-diphenylpenten-3-yne-1 oxide may be explained, apparently, by the influence of the two phenyl radicals upon the reactivity of the acetylenic bond toward bromination. This is borne out by the fact that only two bromine atoms are added to diphenylacetylene, forming the dibromide, no tetrabromide being obtained [7].

EXPERIMENTAL

Synthesis of 1,5-Diphenylpenten-1-ol-3

85 g of phenylacetylene (b.p. 141-144° at 725 mm) was condensed in a Grignard reaction with 113 g of hydrocinnamic acid (b.p. 97-99° at 10 mm), yielding a liquid mass, from which 107 g of a light-yellow, viscous liquid with a b.p. of 181-183° (1 mm) was isolated by double fractional distillation. Yield of the substance was 54.4%, based on phenylacetylene.

d^{20}_{20} 1.0630; n^{20}_{D} 1.5942.

Found: MR_D 75.45.
$C_{17}H_{16}O$. Calculated· MR_D 73.03.

0.3334 g substance; 24.0 g benzene: Δt 0.303°.
Found: M 235.2.
$C_{17}H_{16}O$. Calculated: M 236.0.

0.1224 g substance: 0.3874 g CO_2; 0.0768 g H_2O.
0.1318 g substance: 0.4182 g CO_2; 0.08020 g H_2O.
Found %: C 86.32; 86.54; H 6.97, 6.91.
$C_{17}H_{16}O$. Calculated %: C 86.44; H 6.78.

The synthesized alcohol underwent no visible change during 10 months.

Cleavage of 1,5-Diphenylpenten-1-ol-3 by 15% Caustic Potash

10 g of the alcohol was mixed with three times its volume of 15% KOH and boiled for 5 hours in a flask fitted with a reflux condenser. Ethyl ether was then added to the reaction mass. The lower alkaline layer was separated out, and the upper layer was twice washed with water. This layer, from which the water had been separated, was dried with $CaCl_2$ and then fractionated. Two fractions were obtained: I, with a b.p. of 140-147°, corresponded to phenylacetylene, as was confirmed by its physical properties and its behavior toward an Ag reagent; and II, with a b.p. of 221-227°, corresponding to hydrocinnamic aldehyde.

Thus secondary alcohols behave toward KOH like the tertiary phenylacetylenic alcohols previously investigated by A.E. Favorsky and the authors.

Action of Acetic Anhydride Upon 1,5-Diphenylpenten-1-ol-3

10 g of the alcohol was mixed with twice its volume of acetic anhydride. The mixture was boiled for 10 hours in a flask with a reflux condenser. The acetic anhydride that had not entered into the reaction and the acetic acid that had formed were driven off, and 10 g of a substance with a b.p. of 199-201° (6 mm) was isolated from the residue by double fractionation. Yield of the substance: 85% in terms of the alcohol.

d^{20}_{20} 1.0635; n^{20}_{D} 1.5682.
Found: MR_D 85.53.
$C_{19}H_{18}O_2$. Calculated: MR_D 82.39.

0.4183 g substance: 23.49 g benzene: Δt 0.326°.
Found: M 280.2.
$C_{19}H_{18}O_2$. Calculated: M 278.0.

0.1250 g substance: 0.3768 g CO_2; 0.0748 g H_2O.
0.1198 g substance: 0.3604 g CO_2; 0.0716 g H_2O.
Found %: C 82.21, 82.05; H 6.65, 6.64.
$C_{19}H_{18}O_2$. Calculated %: C 82.02; H 6.48.

The synthesized acetate of 1,5-diphenylpenten-1-ol-3 stood for 10 months in a parrafin-coated test tube without suffering any apparent change during that time.

Dehydration of 1,5-Diphenylpenten-1-ol-3

70 g of the alcohol was mixed with twice its volume of absolute ethyl ether. The ether solution of the alcohol was added in small batches to 50 g of P_2O_5, which was likewise in an anhydrous ether medium. The reaction was accompanied by slight evolution of heat. Twenty-four hours later the mixture was heated with a reflux condenser for one hour over a water bath to the boiling temperature of ether. The ether layer was filtered off, washed twice with water, and dried with K_2CO_3; the ether was then driven off, and 32.5 g of a greenish-yellow liquid with a b.p. of 164-166° (2 mm) was isolated from the residue by double fractional distillation. Yield of the substance: 50.3% in terms of the alcohol.

d_{20}^{20} 1.03154; n_D^{20} 1.6215.
Found: MR_D 74.38.
$C_{17}H_{14}$. Calculated: MR_D 71.035.

0.5323 g substance: 23.6 g benzene: Δt 0.535°.
Found: M 216.3.
$C_{17}H_{14}$. Calculated: M 218.0.

0.1422 g substance: 0.4872 g CO_2; 0.0812 g H_2O.
0.1326 g substance: 0.4550 g CO_2; 0.0761 g H_2O.
Found %: C 93.44, 93.58; H 6.35, 6.38.
$C_{17}H_{14}$. Calculated %: C 93.58; H 6.42.

The ethylenic-acetylenic hydrocarbon 1,5-diphenylpenten-3-yne-1 exhibited no noticeable polymerization upon standing for 8 months. It is a greenish-yellow liquid.

Oxidation of 1,5-Diphenylpenten-3-yne-1 by Acetyl Hydroperoxide

26.4 g of the ethylenic-acetylenic hydrocarbon was oxidized at room temperature (+19°) in an absolute-ether medium by 95 g of 29.3% acetyl hydroperoxide, assuming three oxygen atoms per mole of the hydrocarbon (one oxygen atom for the double bond and two for the triple bond). The reaction proceeded at somewhat higher temperature (+23°). After 11 days the acetyl hydroperoxide that had not entered into the reaction and the acetic acid formed were washed out with water three times. The ether layer with the oxidation product was segregated, dried with K_2CO_3 for 24 hours, and then filtered. The ether was driven off, and fractional distillation (3 mm) of the residue yielded:

Up to 130° — 0.12 g of a crystalline substance:

171-179° – 12 g of a liquid, plus an appreciable tarry residue.

The crystalline substance was recrystallized from CCl_4; it had a m.p. of 118-119°. Owing to the negligible quantity obtained, it was not analyzed further.

Upon repeated distillation of the 171-179° (3 mm) fraction, 8 g of a yellow liquid with a b.p. of 173-174° (2 mm) was isolated. Yield of the substance: 28.2% in terms of the ethylenic-acetylenic hydrocarbon.

d_{20}^{20} 1.0811; n_D^{20} 1.6031.

Found: MR_D 74.35.

$C_{17}H_{14}O$. Calculated: MR_D 70.95.

0.4578 g substance: 23.5 g benzene: Δt 0.43°.

Found: M 232.4.

$C_{17}H_{14}O$. Calculated: M 234.0.

0.1548 g substance: 0.4966 g CO_2; 0.0772 g H_2O.

0.1528 g substance: 0.4890 g CO_2; 0.0866 g H_2O.

Found %: C 87.49, 87.28; H 5.54, 6.29.

$C_{17}H_{14}O$. Calculated %: C 87.18; H 5.98.

The analytical data indicate that the substance under analysis is the oxide of 1,5-diphenylpenten-3-yne-1. It dissolves in ethyl alcohol, ethyl ether, benzene, and chloroform.

A control test under the same conditions was run parallel with the oxidation of the 1,5-diphenylpenten-3-yne-1 by acetyl hydroperoxide. The main and control runs were titrated every day for 11 days with a 0.1 N solution of $Na_2S_2O_3$. This was done by taking 20 ml of the experimental and control solutions, previously dissolved in 250 volumes of water, and determining the amount of unreacted acetyl hydroperoxide iodometrically (Table 2).

TABLE 2

	Milliliters of 0.1 N $Na_2S_2O_3$ used in titrating unreacted acetyl hydroperoxide										
	1 d	2 d	3 d	4 d	5 d	6 d	7 d	8 d	9 d	10 d	11d
Experiment	3.1	2.3	1.8	1.5	1.3	1.2	1.1	1.0	1.0	1.0	1.0
Control	3.1	3.1	3.1	3.1	3.0	3.0	3.0	2.9	2.9	2.9	2.9

It is evident from Table 2 that the oxidation of the 1,5-diphenylpenten-3-yne-1 by acetyl hydroperoxide lasted 7 days, the concentration of the acetyl hydroperoxide remaining unchanged during further titration (4 days). The control run exhibited a negligible change in the concentration of acetyl hydroperoxide during the 11 days.

The oxidation of 26.4 g of 1,5-diphenylpenten-3-yne-1, at the double bond by acetyl hydroperoxide would require 1.938 g of oxygen theoretically, whereas it actually used up 3.382 g of oxygen, as apparent from the amount of acetyl hydroperoxide consumed (Table 2).

Apparently, this is due to the fact that during the oxidation reaction part of the oxygen is used in the further oxidation of the reaction products, forming the tarry residue that we isolated in considerable quantities.

SUMMARY

1. The secondary acetylenic alcohol 1,5-diphenylpentyn-1-ol-3 was synthesized. Its structure was established by its cleavage into phenylacetylene and hydrocinnamic aldehyde, as well as by its conversion into an acetate.

2. Dehydration of 1,5-diphenylpentyn-1-ol-3 yielded the ethylenic-acetylenic hydrocarbon 1,5-diphenylpenten-3-yne-1 with a yield of 50.3%.

3. The acetylenic secondary alcohol 1,5-diphenylpentyn-1-ol-3, its acetate, and the ethylenic-acetylenic hydrocarbon 1,5-diphenylpenten-3-yne-1 proved to be stable compounds. When kept in paraffin-coated test tubes (for 8-10 months) they underwent no apparent changes.

4. The oxide of the hydrocarbon was obtained by oxidizing 1,5-diphenylpenten-3-yne-1 with acetyl hydroperoxide.

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THE CHARACTERISTICS OF α,β-UNSATURATED KETONES. V

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In the course of the research undertaken by us [1] to discover the relationship between the degree of conjugation of the $>C=C<$ and $C=O$ bonds and the chemical properties of the α,β-unsaturated ketones it became necessary to fill in the gaps and to characterize one of the simplest of these ketones, namely, ethylidene acetone.

Ethylidene acetone, which is a close homologue of methyl vinyl acetone, ought to have a very high degree of conjugation of the $>C=C<$ and $C=O$ bonds, and hence its iodoxidation ought to be difficult; the bromination reaction, on the other hand, ought to be quite complete without noticeable evolution of the elements of HBr.

Experimental data on the iodoxidation of ethylidene acetone in an alcohol-water medium indicate that it does not enter into reaction with a 0.1 N. solution of iodine, that the average iodine number is no more than 1.57% of the theoretical value when reacted with a 0.2 N solution of iodine, and that, finally, the average iodine number rises to 2.39% of the theoretical when an approximately 0.5 N iodine solution is used.

Of the homologues of ethylidene acetone, butylidene acetone was also subjected to iodoxidation; the values of the iodine number found were respectively 1.53%, 4.39%, and 17.75% of theory.

Comparison of the experimental data on the iodoxidation of these ketones confirms the conclusion arrived at previously: that as the mass of the aliphatic radical attached to the carbon 1 of the conjugate system: $-\overset{1}{\underset{|}{C}}=\overset{2}{\underset{|}{C}}-\overset{3}{\underset{|}{C}}=\overset{4}{O}$, rises, the degree of conjugation of the $>C=C<$ and $C=O$ bonds diminishes, and the iodoxidation reaction proceeds more completely (Table 1) as a result of the greater independence of the double bond.

Bromination of ethylidene acetone indicates that even with 100% excess of bromine its iodine number averaged 98.02% of theory, and that the reaction proceeded without the formation of hydrogen bromide (Table 2).

TABLE 1

Iodoxidation of Ethylidene Acetone and Butylidene Acetone by Iodine Solutions of Various Concentrations

Test No.	Weight g	Milliliters of 0.1 N solution $Na_2S_2O_3$ required in titrating excess Iodine	milliliters of 0.1 N solution of $Na_2S_2O_3$ corresponding to iodine used	Iodine number	Theoretical iodine number	milliliters of 0.1 N solution of $Na_2S_2O_3$ required to titrate iodine of HI	Conversion of iodine to HI, %
	Ethylidene acetone						
1	0.0960	26.66	–	–	301.98	–	–
2	0.0804	26.66	–	–	301.98	–	–
3	0.1074	47.14	0.39	4.60	301.98	0.03	7.69
4	0.1264	47.04	0.49	4.90	301.98	0.03	6.12
5	0.1686	117.12	0.98	7.38	301.98	0.13	13.26
6	0.1990	116.98	1.12	7.10	301.98	0.18	16.07
	Butylidene acetone						
1	0.0540	26.52	0.14	3.29	224.46	0.01	7.14
2	0.0696	26.44	0.19	3.60	224.46	0.01	5.26
3	0.0862	46.94	0.59	10.15	224.46	0.06	10.16
4	0.0914	46.84	0.69	9.58	224.46	0.07	10.10
5	0.1600	113.15	4.95	39.27	224.46	1.29	26.00
6	0.1146	114.45	3.65	40.42	224.46	0.89	24.39

TABLE 2

Bromination of Ethylidene Acetone in a CCl_4 Medium

Test No.	Weight g	Milliliters of $Br \cdot CCl_4$ solution	Milliliters of 0.1 N solution of $Na_2S_2O_3$ required to titrate excess iodine	Milliliters of 0.1 N solution of $Na_2S_2O_3$ corresponding to iodine used	Overall iodine number	Milliliters of 0.1 N solution of $Na_2S_2O_3$ required to titrate iodine of HI	Substitution iodine number	Addition iodine number
1	0.1141	15.76	33.92	26.67	296.69	–	–	296.69
2	0.1897	24.00	48.03	44.14	295.34	–	–	295.34

Hence, ethylidene occupies the first place in the series of aliphatic α,β-unsaturated ketones of the general type: $R{-}CH{=}CH{-}CO{-}CH_3$ as far as the degree of conjugation of $>C{=}C<$ and $C{=}O$ bonds is concerned.

EXPERIMENTAL

As we know, ethylidene acetone was synthesized by Claisen [2] by dehydrating hydroacetyl acetone. According to Claisen hydroacetyl acetone is prepared with KCN as the condensing agent, its yield not exceeding 25% of theory.

The conversion of the hydroacetyl acetone into ethylidene acetone was effected with a yield of the latter amounting to 30.4% of theory. Hence, when we remember that the yield of hydroacetyl acetone was 25% of theory, even in this case the yield of ethylidene acetone did not exceed 7.6% of theory, in terms of acetaldehyde.

As for the reaction to synthesize ethylidene acetone, we have the comments of E. Kohler [3], who recommended that to increase the yield of ethylidene acetone, the hydroacetyl acetone not be isolated, but that the fraction with a b.p. of 70-90° at 20 mm in crude state be subjected to dehydration by boiling with an equal quantity of acetic anhydride. The improved Kohler method, however, results in a yield of ethylidene acetone that is only 5.9% of theory in terms of acetaldehyde.

In view of the fact that ethylidene acetone is produced with very low yields by the Claisen method, we resolved to condense acetaldehyde with acetone under the conditions for the synthesis of β-ketoles [4] often tested out in our laboratory, in the presence of a dilute aqueous solution of NaOH at 0°.

The reaction was effected in a 2-liter thick-walled jar sealed with a tight-fitting cork with three holes. The holder of the mechanical stirrer passed through the central hole, a dropping funnel through another, and a glass tube with a Bunsen valve through the third hole. The jar thus equipped was placed in a wide vessel full of snow, and 550 ml of acetone and 700 ml of a 1.4% aqueous solution of NaOH previously chilled to 0°, were placed in the jar. Then, with the mechanical stirrer working vigorously, an aqueous solution of acetaldehyde was poured drop by drop from the dropping funnel. The solution of acetaldehyde, prepared from 120 g of freshly prepared CH_3CHO chilled to -21° in 280 ml of ice water was kept at -2° in a freezing mixture and was poured as required into the dropping funnel in tiny batches. It took six hours to add the acetaldehyde solution. Then the reaction mass was set aside overnight at 0°. It was then neutralized with acetic acid and saturated with crystalline table salt. An oily yellowish layer was observed to form; it was segregated, and the rest of the water-acetone liquid was extracted twice with ether. The oily layer and the ether extracts were mixed together and dried with anhydrous Na_2SO_4. After filtering and driving the ether off over a water bath, the residue was heated and a liquid with an end boiling point at 90° was distilled off. A crystal of iodine was added to the residual liquid, and it was then fractionated. The following fractions were isolated: Fraction I, b.p. 90-99° (77 g); Fraction II, b.p. 99-107° (16 g); Fraction III, b.p. 107-176° (89 g); and a tarry residue totalling 35 g.

The 107-176° fraction was redistilled with iodine; the following fractions were obtained: 85-110° fraction (23 g); 110-130° fraction (38 g); 130-168° fraction (16 g); and a tarry residue totalling 11 g.

The fractions with b.p. up to 110° were combined, separated from the water they contained, dried with anhydrous Na_2SO_4, and redistilled, the residue (boiling at above 110°) being 7 g of a liquid that was added to the 110-130° fraction. Subsequent distillation of the 45 g of the 110-130° fraction yielded 38 g of a narrow fraction, corresponding to ethylidene acetone, with a b.p. of 119-121° at 740 mm. The yield of ethylidene acetone in terms of acetaldehyde was 16.6% of theory.

The ethylidene acetone had the following constants:

$$d_4^{20}\ 0.8614;\quad n_D^{20}\ 1.4339.$$

$$\text{Found:}\ MR_D\ 25.40.$$

$$C_5H_8O\,\overline{|}^{=}_{1}.\ \text{Calculated:}\ MR_D\ 24.83.$$

The preparations of ethylidene acetone* underwent iodoxidation, with measured amounts of the ketone dissolved in 20 ml of 96% of alcohol. After 25 ml of an alcoholic solution of iodine had been added and 200 ml of water had been poured in while stirring, the reaction mixture was vigorously agitated and set aside to stand for 5 minutes. The excess iodine was titrated against a 0.1 N solution of hyposulfite, after which 10 ml of 2% KIO_3 was added to compute the HI, and the precipitated iodine again titrated.

Iodoxidation of butylidene acetone was effected in the same manner.

Bromination of the ethylidene acetone was effected with weighed portions dissolved in 10 ml of anhydrous CCl_4 at 0°, which were digested with a Br–CCl_4 solution for 30 minutes.

SUMMARY

1. A practicable method was elaborated for synthesizing ethylidene acetone, which gave a higher and more stable yield of the latter than the Claisen method.

2. We proved that ethylidene has the highest degree of conjugation of the $>C=C<$ and C=O bonds in the aliphatic series of the $R-CH=CH-CO-CH_3$ general type.

3. The rule that with increasing mass of the aliphatic radical attached to the carbon 1 atom of a conjugate system the independence of the ethylenic linkage increases in α,β-unsaturated ketones was confirmed.

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* Up to now two runs have been made.

RESEARCH IN THE DECALIN SERIES

V. IRREVERSIBLE CATALYSIS OF DECALIN HYDROCARBONS WITH UNSATURATED SIDE CHAINS

R. Y. Levina and S. G. Kulikov

Moscow State University Awarded the Order of Lenin.
Laboratory of Organic Chemistry named after Academician N. D. Zelinsky

In previous papers by one of the present authors [1] it was shown that cyclohexane hydrocarbons with unsaturated side chains undergo an irreversible transformation of the type of N.D. Zelinsky's irreversible catalysis upon contact with platinum or palladium at 200° in a gentle current of carbon dioxide. The products of catalysis were a mixture of aromatic and cyclohexane hydrocarbons with corresponding saturated side chains:

$$3C_6H_{11}(CH_2)_nCH{=}CH_2 \longrightarrow C_6H_{11}(CH_2)_nCH_2CH_3 + 2C_6H_5(CH_2)_nCH_2CH_3.$$

The contact transformation of these hydrocarbons was complete even with one pass over the platinum or palladium, no matter how far from the ring the multiple bond (double or triple) happened to be.

In the present research we undertook to investigate the contact transformations of the decalin hydrocarbons with unsaturated side chains, containing a double bond at varying distances from the ring.

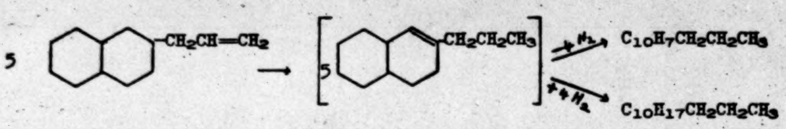
It was of some importance to determine whether the decalins with unsaturated side chains behave like the cyclohexanes with similar side chains under the conditions of irreversible catalysis, as well as whether the process of irreversible catalysis is affected by the distance of the double bond from the ring and the steric structure of the bicyclic decalin system.

To resolve these questions the stereoisomeric β-allyldecalins: (3-β-cis-decalylpropene-1 and 3-β-trans-decalylpropene-1 and β-decalylbutenes (4-β-cis-decalylbutene-1 and 4-β-trans-decalylbutene-1), were subjected to contact with platinized charcoal.

It was found that in a single pass over the catalyst both β-allyldecalins, undergo complete transformation – there is none of the initial unsaturated hydrocarbons in the catalysis products (by the reaction with bromine water).

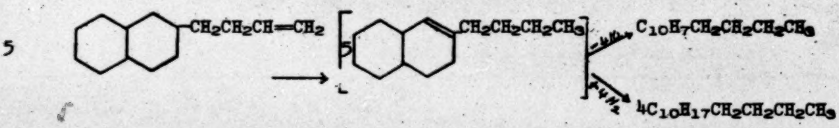
If the dehydrogenation process had affected only one ring of the input bicyclic hydrocarbon in the irreversible catalysis, the catalyzate would contain tetralin and decalin hydrocarbons in the proportion of 1:2. If the dehydrogenation process affected both rings of the input hydrocarbon, the catalyzate would be a mixture of naphthalene and decalin hydrocarbons in the proportion of 1:4.

The results obtained in treating the products of catalysis with sulfuric acid justify the assumption (on the basis of the amount of hydrocarbon reacting with the sulfuric acid) that the process of irreversible catalysis of both stereoisomeric β-allyldecalins follows the latter path:

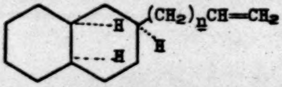


As evident from the above equation, the first step of the reaction is the contact isomerization[1] of the input β-allyldecalins to β-propyloctalins (cis and trans), which are in turn subjected to irreversible catalysis, forming a mixture of β-propylnaphthalene and the corresponding β-propyldecalin (cis and trans), just as trans octalin [3] easily undergoes conversion over palladium into a mixture of naphthalene and trans decalin.

Removing the double bond still farther from the ring than is the case in the β-allyldecalins does not complicate the process of irreversible catalysis of decalin hydrocarbons with unsaturated side chains: 4-β-decalinbutene-1 (cis and trans) undergoes complete transformation in a single pass over platinized charcoal, forming β-butylnaphthalene and the corresponding β-butyldecalins (cis and trans):



Our experimental data indicated that the stereoisomeric (cis and trans) hydrocarbons of the decalin series



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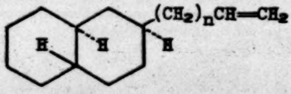
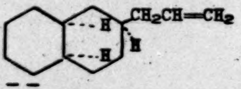


exhibit no difference in their behavior under irreversible catalysis.

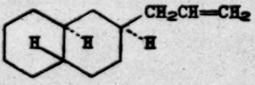
EXPERIMENTAL

1. Irreversible Catalysis of Stereoisomeric β-Allyldecalins

The synthesis and constants of β-allyl-cis-decalin and β-allyl-trans-decalin have been described in one of our previous reports [5]. Both β-allyldecalins:



and



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[1] The presence of the stage of catalytic isomerization (with a shift of the double bond from the side chain to the ring) in the process of irreversible catalysis of six-membered ring hydrocarbons with unsaturated side chains was demonstrated experimentally by one of the present authors [4] in earlier papers.

cis-isomer: b.p. 109° (12 mm); n_D^{20} 1.4888; d_4^{20} 0.8971; trans isomer: b.p. 106° (13 mm); n_D^{20} 1.4820; d_4^{20} 0.8808.

were passed over platinized charcoal (25 Pt) under the conditions of N.D. Zelinsky's irreversible catalysis [2]: at 200-205°, in a gentle current of carbon dioxide, and at a speed of 0.1 ml per minute (length of the catalyst layer-25 cm; tube diameter - 10 mm). The catalysis products obtained were treated, with agitation and chilling, first with monohydrated sulfuric acid and then with fuming sulfuric acid (7%SO_3). Of every 5 ml of each catalyzate, 1 ml was reacted with sulfuric acid. The remaining layers of the hydrocarbons (4 ml each), were washed with water, soda, and again water until their reaction was neutral, then dried with calcium chloride and distilled in vacuum (with a Vaigret dephlegmator) over sodium. Thus there were isolated: β-propyl-cis-decalin from the products of the irreversible catalysis of β-allyl-cis-decalin, and β-propyl-trans-decalin from the products of the irreversible catalysis of β-allyl-trans-decalin. The constants of these stereoisomeric β-propyldecalins:

cis isomer: b.p. 100° (5 mm); n_D^{20} 1.4771; d_4^{20} 0.8836; MR_D 57.72; $C_{13}H_{24}$ calculated MR_D 57.83.

trans isomer: b.p. 95-96° (7 mm); n_D^{20} 1.4711; d_4^{20} 0.8658. MR_D 58.26; $C_{13}H_{24}$ calculated MR_D 57.83. EM_D 0.43.

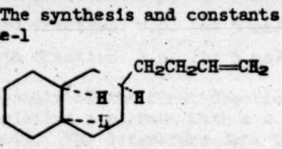
coincide precisely with the constants of the hydrocarbons synthesized by the hydrogenation of the stereoisomeric β-allyldecalins and described by us in one of our previous reports [5].

Owing to the small amount of hydrocarbon sulfonated (2 ml in both tests), we were unable to isolate β-propylnaphthalene from the sulfuric-acid layer in sufficiently pure form: when the sulfo acid was hydrolyzed with water (by Kinzher's method [7], we got 0.3 g of a hydrocarbon that had a n_D^{20} 1.5863 after distillation in vacuum. As the synthesis and constants of β-propylnaphthalene are not described in the literature, we had to produce it by the catalytic dehydrogenation of β-propyldecalin; the β-propylnaphthalene thus synthesized (cf. Section 3) had a n_D^{20} 1.5922.

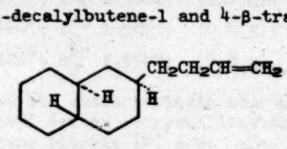
Thus, the β-propyldecalins (cis and trans) were isolated by the irreversible catalysis of the β-allyldecalins and defined by their constants. The presence of β-propylnaphthalene in the catalysis products was demonstrated in both cases by reaction with sulfuric acid and by the closeness of the refractive index of the hydrocarbon produced by the hydrolysis of the sulfo acid to the refractive index of β-propylnaphthalene.

2. Irreversible Catalysis of the Stereoisomeric β-Decalylbutenes

The synthesis and constants of 4-β-cis-decalylbutene-1 and 4-β-trans-decalylbutene-1



and



are described in one of our previous reports [7]. Both of the β-decalylbutenes:

cis-isomer: b.p. 125-126° (12 mm); n_D^{20} 1.4870; d_4^{20} 0.8936; trans isomer:

b.p. 121-122° (12 mm); n_D^{20} 1.4803; d_4^{20} 0.8782,

were passed over platinized charcoal (25% Pt) under the conditions described above (200-205°, gentle current of carbon dioxide, and 0.1 ml per minute). The products of catalysis did not bleach bromine water. Both catalyzates were treated with monohydrated sulfuric acid and then with fuming sulfuric acid (7% SO_3). Of 6 ml Catalyzate I 1.1 ml reacted with sulfuric acid; of 4.8 ml of Catalyzate II, 0.9 ml reacted with sulfuric acid. The remaining hydrocarbon layers (4.9 ml and 3.9 ml) were washed to a neutral reaction, dried with calcium chloride, and distilled in vacuum (with a Vigret dephlegmator) over sodium. This isolated β-butyl-cis-decalin from the products of the irreversible catalysis of 4-β-cis-decalylbutene-1, and β-butyl-trans-decalin from the products of the irreversible catalysis of 4-β-trans-decalylbutene-1.

The constants of the stereoisomeric β-butyldecalins:

cis isomer: b.p. 123-124° (12 mm); n_D^{20} 1.4775; d_4^{20} 0.8799; MR_D 62.39; $C_{14}H_{26}$ calculated MR_D 62.45;

trans isomer: b.p. 118.5-119° (12 mm); n_D^{20} 1.4710; d_4^{20} 0.8643; MR_D 62.83; $C_{14}H_{26}$ Calculated MR_D 62.45; EM_D 0.38,

coincide precisely with the constants of the hydrocarbons synthesized by the hydrogenation of the corresponding β-decalylbutenes and described by us in one of our previous reports [7].

Thus, the β-butyldecalins (cis and trans) were isolated from the products of irreversible catalysis and defined by their constants. The presence of β-butylnaphthalene in both products of catalysis was proved by their reaction with sulfuric acid.

3. Catalytic Dehydrogenation of the β-Propyldecalins

Both of the β-propyldecalins (cis and trans), whose constants have been cited above (*cf.* Section 1), were separately subjected to catalytic dehydrogenation over platinized charcoal at 305°, in a gentle current of carbon dioxide and at a rate of 0.15 ml per minute. The products of catalysis had a n_D^{20} of 1.5600 and 1.5570; after a second pass over the same catalyst (the activity of which was checked by the dehydrogenation of cyclohexane) two new catalyzates were obtained with identical refractive indexes: n_D^{20} 1.5602 and 1.5600. They were combined (10 g) and subjected to double fractionation (with a Vigret dephlegmator) in vacuum; the following fractions were collected:

1st fraction: b.p. (at 5 mm) up to 85°; crystals (0.5 g);
2nd fraction: b.p. (at 5 mm) 85-115°; n_D^{20} 1.5082; (1.6 g);
3rd fraction: b.p. (at 5 mm) 115-120°; n_D^{20} 1.5825; (0.6 g);
4th fraction: b.p. (at 5 mm) 120-121°; n_D^{20} 1.5940; (6.8 g).

The crystals of the first fraction, which had the characteristic odor of naphthalene, yielded a picrate with a m.p. of 148-149° (after recrystallization from methanol). The literature data for naphthalene picrate [8] are: m.p. 149°.

From these data it could be assumed that the dehydrogenation of the β-propyldecalins is accompanied by a partial rupture of the side chain (the naphthalene constituted 5% by weight of all the fractions of the catalyzate).

The second and third fractions, which were of small size and apparently consisted of a mixture of β-propyl-naphthalene and the initial β-propyldecalins to judge by the refractive indexes (with the propylnaphthalene predominating in the third fraction) were not investigated further.

The forth fraction was treated with steam to remove any possible traces of naphthalene, only a few drops of oil being driven off, however. The hydrocarbon that remained in the distilling flask was extracted with ether, dried with calcium chloride, and, after the ether had been driven off, again distilled in vacuum; it distilled over completely (6 g) within a single degree of temperature and possessed the following constants:

B.p. 120-121° (6 mm); n_D^{20} 1.5922; d_4^{20} 0.9854; MR_D 58.43 $C_{13}H_{14}\Gamma_5$.
Calculated MR_D 55.5; EM_D 2.93.
0.1347 g substance: 0.4522 g CO_2; 0.0561 g H_2O.
Found %; C 91.58; H 8.46.
$C_{13}H_{14}$. Calculated %: C 91.71; H 8.29.

Judging by the constants of the hydrocarbon produced, by the exaltation of its molecular refraction (characteristic of the homologues of naphthalene [9]), and by the data of analysis, we could assume that it was pure β-propylnaphthalene. Its structure was confirmed by the preparation of its picrate. The picrate of β-propylnaphthalene (from methanol), which settled out only after two months of standing, consisted of bright orange crystals with a m.p. of 93-94°.

The table below provides a comparison of the constants of the β-propylnaphthalene first synthesized by us (as follows: β-chlorodecalin ⟶ β-allyl decalin ⟶ β-propyldecalin ⟶ β-propylnaphthalene) with the only data reported in the literature for this hydrocarbon, as well as with the constants of its isomers: isopropylnaphthalene and α-propylnaphthalene.

Hydrocarbon	Method of Synthesis	B.p. °C	n_D^{20}	d_4^{20}	EM_D	M.p. of picrate	Author
β-propyl-naphthalene	Dehydrogenation of β-propyldecalin (cis and trans)	120-121 (6 mm)	1.5922	0.9854	2.93	93-94	present report
	Pyrogenic decomposition of phenanthrene.	260-275 (decomp)	–	0.991 d_0^{25}	–	–	N.A. Orlov[10]
Isopropyl-naphthalene	Action of isopropylsulfuric acid on naphthalene	260-265	1.5881	0.9852	2.7	–	A.D.Petrov and assoc[11]
α-Propyl-naphthalene	Catalytic hydrogenation of α-allyl-naphthalene	114-115 7 mm	1.5928	0.9904	2.69	88-90	R.Y.Levina and Assoc.[12]

SUMMARY

1. The process of irreversible catalysis (over platinized charcoal) of

β-allyldecalin, β-allyl-trans-decalin, 4-β-cis-decalylbutene-1, and 4-β-trans-decalylbutene-1 was studied.

2. It was established that the irreversible catalysis of these decalin hydrocarbons with ethylenic side chains proceeds to completion, no matter what the steric (cis or trans) structure of the decalin system or the distance of the double bond from the ring.

3. The products of the irreversible catalysis of the stereoisomeric decalin hydrocarbons with ethylenic side chains are naphthalene and stereoisomeric decalin hydrocarbons with the corresponding saturated side chains.

4. Thus, the hydrocarbons of the decalin series with ethylenic side chains behave like their analogues among the cyclohexanes during irreversible catalysis.

5. Individual β-propylnaphthalene, characterized for the first time by its constants and by the preparation of its picrate, was synthesized by the catalytic dehydrogenation of the β-propyldecalins (cis and trans).

6. It was shown that the partial (5%) splitting off of a side chain and the formation of naphthalene also occur during the catalytic dehydrogenation of the β-propyldecalins.

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THE SYNTHESIS OF SOME HOMOLOGUES AND N-SUBSTITUTED DERIVATIVES OF PYRROLE AND PYRROLIDINE

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Moscow State University named after M. V. Lomonosov and awarded the Order of Lenin.
Laboratory of Organic Chemistry named after Academician N. D. Zelinsky.

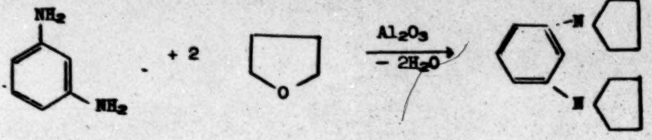
The present report deals with the synthesis of some homologues and N-substituted derivatives of pyrrole and pyrrolidine by the conversion of oxy heterocyclic compounds into rings with different heterocyclic atoms [1]. In the pyrrole series N-*n*-amylpyrrole and α-ethylpyrrole were synthesized; and in the pyrrolidine series, N-allylpyrrolidine, N-*n*-amylpyrrolidine, N-cyclopentylpyrrolidine, di-N,N'-pyrrolidinethane, m-phenylene-di-N,N'-pyrrolidyl, and α-ethylpyrrolidine.

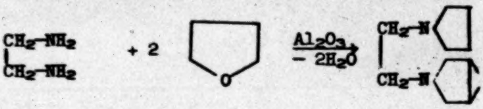
The yield of the N-substituted derivatives of pyrrole drops appreciably as the number of carbon atoms in the input amine increases: N-ethylpyrrole was synthesized with a yield of 27% [2], whereas the yield of N-*n*-amylpyrrole does not exceed 14% of the theoretical. In the synthesis of N-substituted derivatives of pyrrolidine, increasing the number of carbon atoms in the input amine does not affect the yield of the reaction products, the N-n-amylpyrrolidine being obtained with a yield that was 55% of the theoretical.

Reduction of the yield of reaction products, due to an increase in the number of carbon atoms in the side chain of the initial oxyheterocyclic compounds, is also observed in the synthesis of the α-alkyl homologues of pyrrole and pyrrolidine: α-methylpyrrole was synthesized with a yield of 24% [3], whereas the yield of α-ethylpyrrole was 5%; the yield of α-methylpyrrolidine was 27% [4], whereas that of α-ethylpyrrolidine was 9% of the theortetical.

It should be noted that the reaction of allylamine with furanidine (tetrahydrofuran) results in the formation of N-allylpyrrolidine, but with a considerably lower yield than was the case in the reaction between benzylamine and furanidine, where the yield of N-benzylpyrrolidine was 30% [5]. N-Allylpyrrolidine was isolated as the picrate from the mixture of reaction products in the present research.

The reaction of furanidine with diamines resulted in the synthesis of compounds containing two pyrrolidine rings per molecule:





EXPERIMENTAL

1. N-n-Amylpyrrole. 12 g of furan mixed with 17 g of n-amylamine were passed at a rate of 8-10 drops per minute in a current of nitrogen through a tube filled with Al_2O_3 and heated to 465-470°.

Double distillation of the dried reaction product yielded 3.4 g of N-n-amylpyrrole (yield: 14% of the theoretical):

B.p. 95-96° (28 mm); d_4^{20} 0.8643; n_D^{20} 1.4731;

MR_D 44.51; $C_9H_{15}N\bar{F}_2$. Calculated: MR_D 44.58.

Found %: N 10.13, 10.18.

$C_9H_{15}N$. Calculated %: N 10.21.

A pinewood chip wetted with hydrochloric acid was turned purplish red by the vapors of N-n-amylpyrrole.

Literature data for N-n-amylpyrrole [6]

B.p. 180-184° (760 mm); d_4^{10} 0.8786.

2. α-Ethylpyrrole. 8 g of α-ethylfuran was passed over Al_2O_3 at a rate of 6 drops per minute in a strong current of ammonia at 450°. After triple distillation of the dried catalyzate, 0.4 g of α-ethylpyrrole was obtained (yield: 5% of the theoretical):

B.p. 164-165° (754 mm); d_4^{20} 0.9042. n_D^{20} 1.4942;
MR_D 30.61. $C_6H_9N\bar{F}_2$. Calculated: MR_D 30.37.

A pinewood chip wetted with hydrochloric acid turned purplish red in the vapors of α-ethylpyrrole.

5.179 mg substance: 0.656 ml N_2 (15°, 742 mm).
7.483 mg substance: 0.952 ml N_2 (15°, 743 mm).
Found %: N 14.66, 14.74.
C_6H_9N. Calculated %: N 14.72.

Literature data for α-ethylpyrrole [7]:

B.p. 163-165°; [8]: b.p. 163-165°.

3. N-Allylpyrrolidine. 18 g of furanidine mixed with 14.4 g of allylamine were passed over Al_2O_3 at 400° in a current of nitrogen at a rate of 6-8 drops per minute. After the ether had been driven off, fractionation of the dried ether extract of the catalyzate yielded a fraction that boiled over in the 90-135° range. A considerable amount of tarry residue remained in the distillation flask.

The addition of an ether solution of picric acid to the 90-135° fraction precipitated a picrate, which melted at 141° after recrystallization from alcohol, and proved to be the picrate of N-allylpyrrolidine.

2.315 mg substance: 0.336 ml N_2 (18°, 746 mm).
Found %: N 16.71
$C_{13}H_{16}O_7N_4$. Calculated %: N 16.52

Literature data for N-allylpyrrolidine:

No N-allylpyrrolidine was obtained in the free state; its chloroaurate, with a m.p. of 97-98° and its chloroplatinate, with a m.p. of 205°, are described [9].

4. N-n-Amylpyrrolidine. 7 g of furanidine and 9.7 g of n-amylamine were passed over Al_2O_3 together at a rate of 8-10 drops per minute and at 390°; after suitable treatment of the catalyzate and repeated distillation 7.5 g of N-n-amylpyrrolidine was obtained with a yield of 55% of the theoretical:

B.p. 81-82° (28 mm); d_4^{20} 0.8191; n_D^{20} 1.4439;
MR_D 45.77. $C_9H_{19}N$. Calculated MR_D 45.50.

The melting point of the picrate was 117.5-118° after recrystallization from alcohol:

Found %: N 9.88, 9.85.
$C_9H_{19}N$ Calculated %: N 9.91.

Literature data for N-n-amylpyrrolidine:

B.p. 179° (760 mm); m.p. of picrate 118-119° [10]; b.p. 89-94° (28 mm)
d_4^{20} 0.8216; n_D^{20} 1.4428 [11].

5. N-Cyclopentylpyrrolidine. A mixture of 5 g of furanidine and 5.6 g of cyclopentylamine was passed over Al_2O_3 at 400° at a rate of 6 drops per minute in a current of nitrogen. After suitable treatment of the catalyzate, repeated distillation of the latter yielded 3.9 g of N-cyclopentylpyrrolidine with a yield that was 40% of the theoretical:

B.p. 91-92° (28 mm); d_4^{20} 0.8992; n_D^{20} 1.4744;
MR_D 43.47 $C_9H_{17}N$. Calculated: MR_D 43.30.

The melting point of the picrate was 149.5-150°.

Found %: N 10.01, 10.04.
$C_9H_{17}N$. Calculated %: N 10.08.

N-cyclopentylpyrrolidine is not described in the literature.

6. Di-N,N'-pyrrolidylethane. 36 g of furanidine mixed with 10 g of ethylenediamine (3:1) were passed over Al_2O_3 in a weak current of nitrogen at 400°. 1.3 g of di N,N'-pyrrolidylethane was isolated from the catalyzate:

B.p 151-152° (750 mm); d_4^{20} 0.9860; n_D^{20} 1.4715.

4.731 mg substance: 0.678 ml N_2 (20°, 754 mm).
4.197 mg substance: 0.599 ml N_2 (20°, 754 mm).
Found %: N 16.58, 16.51.
$C_{10}H_{20}N_2$. Calculated %: N 16.66.

Di-N,N'-pyrrolidylethane is a yellow oil with a sharp odor, causing a strong headache; it is not described in the literature.

7. m-Phenylene-di-N,N'-pyrrolidyl. A mixture of 20 g of furanidine and 10 g of m-phenylenediamine (2.7:1) was passed over Al_2O_3 at 400° in a weak current of nitrogen. Double fractionation of the catalyzate, which had been dried with caustic potash, yielded 2.8 g of m-phenylene-di-N,N'-pyrrolidine:

B.p. 137-139° (8 mm); d_4^{20} 1.071; n_D^{20} 1.5910;
MR_D 67.07; $C_{14}H_{20}N_2F_3$. Calculated: MR_D 66.75.

The melting point of the picrate was 126-127° after recrystallization from alcohol.

3.268 mg substance: 0.369 ml N_2 (18°, 750 mm).
4.336 mg substance: 0.482 ml N_2 (18°, 750 mm).
Found %: N 12.90, 12.87.
$C_{14}H_{20}N_2$. Calculated %: N 12.91.

m-Phenylene-di-N,N'-pyrrolidine is not described in the literature.

8. α-Ethylpyrrolidine. 10.2 g of α-ethylfuranidine was passed over Al_2O_3 at 400° at a rate of 6-7 drops per minute in a strong current of ammonia. The catalyzate yielded 0.9 g of α-ethylpyrrolidine (yield: 9% of the theoretical:

B.p. 122-123° (752 mm); d_4^{20} 0.8395; n_D^{20} 1.4420.
MR_D 31.25. $C_6H_{13}N$. Calculated: MR_D 31.30.

The melting point of the picrate was 84-85° after recrystallization from alcohol.

Found %: N 14.01, 14.05.
$C_6H_{13}N$. Calculated %: N 14.10.

Literature data for α-ethylpyrrolidine:

B.p. 122.4° (744 mm); d_4^{15} 0.844; n_D^{15} 1.4442.
M.p. of picrate 85° [12]; b.p. 110-120°; n_D^{15} 1.4256 [13].

SUMMARY

It has been established in the present paper that the catalytic conversion of oxy heterocyclic compounds into nitrogen heterocyclic compounds may be employed to synthesize compounds that contain two pyrrolidine rings in their molecule.

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REACTIONS OF ALIPHATIC DIAZO COMPOUNDS WITH UNSATURATED COMPOUNDS

1. Mechansim of the Reactions

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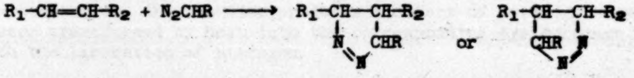
Aliphatic diazo compounds can react with ethylenic bonds in two ways: either they are directly attached to the double bond, forming pyrazolines, or liberate nitrogen in these reactions and form nitrogen-free compounds with the olefins: derivatives of cyclopropane or homologues of the olefins.

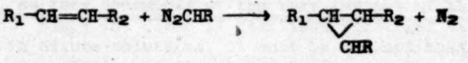
Accordingly, the following equations may be written for these reactions:

Class I: Reactions in which no Nitrogen is Liberated

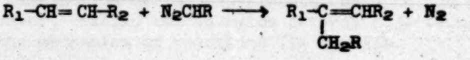


Class II: Reactions in which Nitrogen is Liberated:

II a. The reaction products are derivatives of cyclopropane:

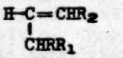


II b. The reaction products are homologues of the olefins:



$$R_1{-}CH{=}CH{-}R_2 + N_2CHR \longrightarrow R_1{-}\underset{CH_2R}{C}{=}CHR_2 + N_2$$

and other derivatives, such as



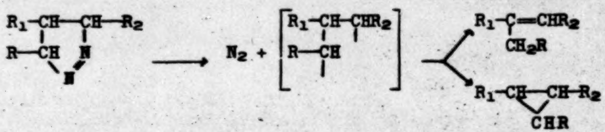
$$H{-}\underset{CHRR_1}{C}{=}CHR_2$$

II c. The reactions of Equations (IIa) and (IIb) may proceed simultaneously.

The symbols R, R_1, and R_2, which apply to each of these equations independently of the others retain their own significance of radicals or atom groups. A shift from one method of reaction to another within this classification may be motivated not only by a change in the experimental conditions, but – in some cases – likewise by a simple change in the nature of these radicals.

The mechanism of the Class I reactions were discussed earlier by the author in the pages of this journal in connection with experimental research undertaken in this field [1,2]. We propose to deal with the problem of the mechanism of the Class II reactions in the present paper, insofar as this can be done with the experimental results achieved by the author or known from the literature.

As we know [3], the products of Class II reactions are mostly formed in the decomposition of the derivatives of pyrazoline that may be synthesized from the same initial components by Equation I.



Pyrazoline is decomposed by heat. Sometimes catalysts are employed [4].

For example, in Buchner's experiments with ethyl diazoacetate and esters of unsaturated acids, the reaction products – esters of pyrazoline carboxylic acids – were transformed by heat into the corresponding cyclopropane derivatives with the liberation of nitrogen.

It was naturally assumed that the pyrazolines were also the intermediate products of the reactions in which cyclopropanes or homologues of the olefins (IIa and IIb) are formed. The elusiveness of the pyrazolines in these cases is due to their specific instability, which is caused by the peculiarities of their structure, as they decompose at the very instant of their formation, liberating nitrogen. Since the Class II reactions sometimes take place at room temperature and in dilute solutions, it must be assumed that the origin and cleavage of the pyrazolines can also take place under these conditions.

Critical examination of the experimental data on the decomposition of the pyrazolines, however, enables one to raise several objections to this point of view regarding the mechanism of reactions IIa and IIb.

First of all, not all the pyrazolines decompose with the evolution of nitrogen upon heating. According to Auwers [5], pyrazolines that have no carboxyl groups in the ring (pyrazolines of simple structure) generally do not tend to undergo this decomposition. Moreover, the same author concludes, on the basis of adequate experimental data, that the presence of a single carboxyl group in the ring makes this reaction more likely, though the decomposition products are, as a rule, acyclic compounds (IIb)[1]. Only when two carboxyl groups are present can Reaction (IIa) take place, resulting in the synthesis of cyclopropanes, though even here a mixture of cyclic and acyclic derivatives

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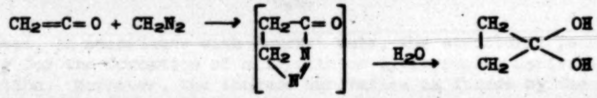
[1] See footnote on following page.

(IIb) is often formed[2].

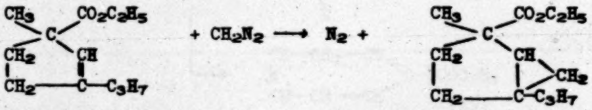
Is Auwer's rule applicable to the decomposition of the pyrazolines whose formation is assumed during the course of Reactions IIa and IIb? The following examples of these reactions may convince us to the contrary.

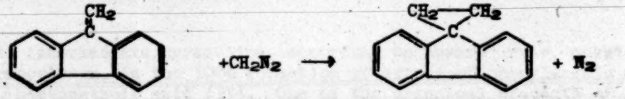
In the well-known experiments by Lipp [6] to synthesize cyclopropanone, ketene and diazomethane were reacted together in the cold, the ether immediately liberating nitrogen when exposed to moisture:



If, in agreement with some authors [7], we assume this kind of diagram for the reaction, the 3(5)-pyrazolone within the brackets ought to be the intermediate product of this reaction. But 3(5)-pyrazolone in no way possesses the properties of a compound that decomposes in the cold in a dilute solution, liberating nitrogen.

In the light of Auwer's rule on the decomposition of the pyrazolines, it might be thought that in syntheses with diazomethane, resulting in formation of an ester of thujanecarboxylic acid [8] or in the formation of trimethylene fluorene [9], another improbable formation might occur – the cleavage of the intermediate pyrazolines:





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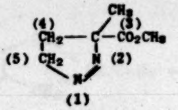
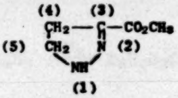
[1] But some details of the structure of the pyrazolines may, according to Auwers, lead to regular departures from this general rule. For instance, decomposition of the ester of the methyl-substituted pyrazolinecarboxylic acid (I) yields a mixture of cyclic and acyclic esters, whereas its unsubstituted analogue (II)



(I) Δ_1-pyrazoline

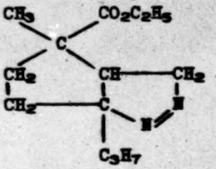


(II) Δ_2-pyrazoline

decomposes, forming 100% of an acyclic ester. The first pyrazoline belongs to the Δ_1 series, and upon decomposition forms the „$-CH_2-CH_2-C(CH_3)CO_2CH_3-$" group, which stabilizes immediately to cyclopropane. The shift to the most favorable system (because of the configuration) of Δ_2-pyrazoline is impeded here by the presence of methyl at the third carbon atom of the ring.

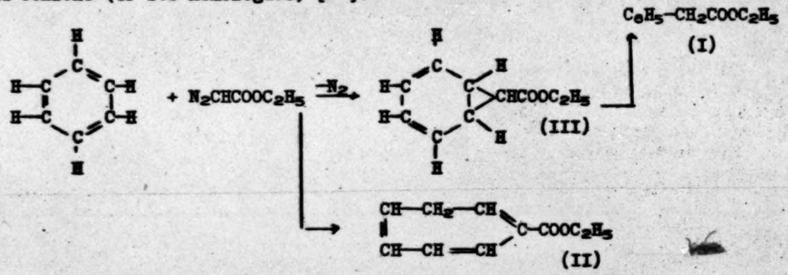
[2] What is characteristic of dicarboxylic acids is the formation of acyclic esters whenever the cyclopropanes produced by the decomposition of the pyrazolines prove to be unstable, immediately isomerizing into olefins (for example, gem-atom groups attached to one of the ring's carbon atoms).

Thus, for example, the pyrazoline formed from



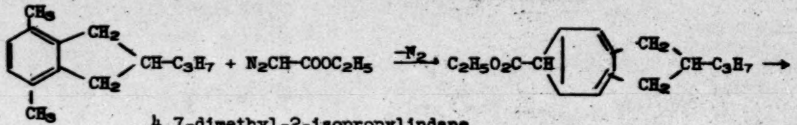
does not possess, in accordance with Auwers' rule, the structural peculiarities necessary for the formation of alicyclic or cyclopropane derivatives upon its decomposition. Moreover, the thujane derivative is formed by the action of CH_2N_2 in the cold and in a dilute ether solution.

Nor can the formation of the pyrazolines as intermediate conversion products be supposed for the well-known Buchner syntheses with ethyl diazoacetate and benzene (or its homologues) [10]:

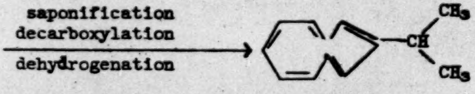


The intermediate pyrazoline, according to Auwers' rule, ought to result, upon decomposition, in the 100% formation of esters of phenylacetic acid (I) or of cycloheptanetroic acid (II). One of the principal products of the reaction, however, is the ester of norcaradienecarboxylic acid (III).

The same must be said of the mechanism of the reaction that results in the synthesis of a derivative of azulene [11].

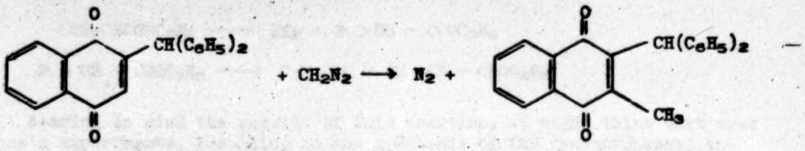


4,7-dimethyl-2-isopropylindane

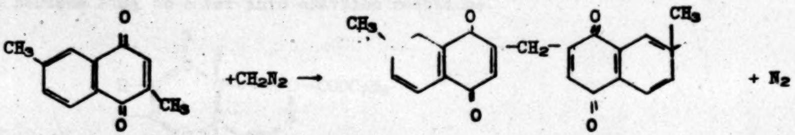


4,8-dimethyl-2-isopropylazulin

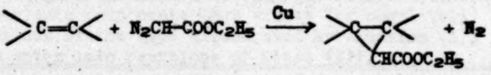
We could also cite an example that is in poor agreement with the hypothesis of the intermediate formation of the pyrazolines, according to Auwers' general rules, for reactions of Class (IIb) as well [12]:



If we might still consider the question of the intermediate formation of pyrazoline in this reaction, the reaction of 3,7-dimethyl-α-naphthoquinone with diazomethane, resulting in the synthesis of dimethyldinaphthylquinonemethane, must no doubt be of a different kind:



New experimental data, testifying to the inapplicability of the hypothesis of the intermediate formation of pyrazolines in reactions of Class II, is furnished us by Loos's experiments [13] with ethyl diazoacetate in the presence of powdered copper. To a certain degree the Loos reaction is analogous to the Sandmeyer reaction in the aromatic series, resulting in the formation of cyclopropane derivatives when the ethyl diazoacetate acts on the ethylenic bond in the presence of copper bronze ('' Natur Cupfer C''):



Unfortunately, this reaction was tried on only a small number of objects by the author himself, and subsequently was used but little in the synthesis of cyclopropane derivatives.

Loos [13] showed that the reaction between ethyl diazoacetate and benzene, effected by Buchner with prolonged heating of both constituents in a sealed tube, is very easy and smooth when the ethyl diazoacetate is added drop by drop to the boiling benzene, in which there is the finest possible suspension of copper bronze. The addition of each new portion of ethyl diazoacetate to the reaction mixture gives rise to the liveliest evolution of nitrogen and is accompanied by the evolution of a small quantity of heat. This reaction results in the formation of the same products as in Buchner's reaction, in addition to a fumarate.

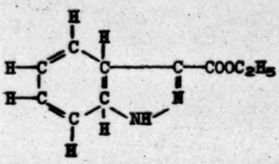
Ethyl diazoacetate reacts analogously in a ligroin medium with α-pinene as well as with camphene.

If ethyl diazoacetate is heated by itself in a suitable (inert) solvent in the presence of copper powder, it is found that the fumarate is formed, evidently because of the decomposition of the diazo components as follows:

$$2N_2CHCOOC_2H_5 \longrightarrow 2N_2 + 2 > CH - COOC_2H_5$$

$$2 > \underset{\bullet}{C}H - COOC_2H_5 \longrightarrow C_2H_5OOC - CH = CH - COOC_2H_5$$

Bearing in mind the results of this reaction, we might think that even in Loos's experiments, resulting in the synthesis of the cyclopropanes, the first act of the reaction is the decomposition of the diazo components in accordance with Equation III (or of an unstable complex of both constituents of the reaction), and not the formation of pyrazoline derivatives. This conclusion is all the more plausible because when the reaction is effected with benzene, for example, the supposition regarding the formation of a pyrazoline derivative becomes quite improbable owing to the almost complete inability of the benzene ring to enter into addition reactions.



In fact, formation of the pyrazoline ester of the indicated structure has never been observed, since the reaction products in all of Buchner's and Loos's reactions were compounds containing no nitrogen.

In view of what has just been said it seemed to us to be not without interest, in evaluating the mechanism of the Loos-Buchner reactions, to search for still other ethylenic components that almost (or completely) lack an ability to enter into reactions of the type illustrated by Equation (1), though retaining the ability to enter into reactions of Class (II).

We selected as the subjects of investigation that were closest at hand the simple vinyl ethers and vinyl acetate, of the general formula,

$$CH_2{=}CH{-}OR$$

where $R = C_4H_9,\ C_2H_5$ and $COCH_3$

The nucleophilic nature of these reagents, depending, as already stated [2], upon the superposition of the

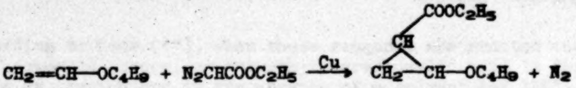
$$CH_2{=}CH{-}CR \longleftrightarrow \bar{C}H_2{-}CH{=}\overset{+}{O}R$$

structures, governs the passive nature of these ethylenic linkages toward addition reactions as well as those imparted by the nucleophilic properties. As was indicated earlier, diazomethane and ethyl diazoacetate are such substances.

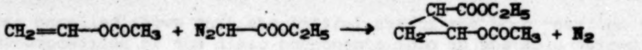
It was shown by the authors of this paper, moreover, that diazomethane is really not added in ether solution to the double bond of vinyl ether.

Further research indicated that ethyl diazoacetate does not react with vinylbutyl ether either, even after prolonged heating of both constituents at 100°.

A corresponding experiment also showed that the Loos reaction proceeds easily and smoothly between ethyl diazoacetate and vinyl butyl ether at the boiling point of the ether (93°):

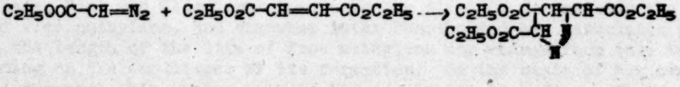


The product of the reaction is obtained in a yield that is 80% of the theoretical; it represents the nearly pure cyclopropane ether with only a slight trace (2%) of unsaturated isomers. A detailed description of the reaction conditions and the investigation of the end products will be given in our next report. An ester of cyclic structure was likewise synthesized by the action of ethyl diazoacetate upon vinyl acetate in the presence of copper:



In this case, too, the intermediate formation of a pyrazoline derivative appears hardly likely, in view of the nucleophilic nature of both ingredients in the reaction[1].

It must be concluded from all that has been said above that the hypothesis involving the idea of the intermediate formation of pyrazolines in Class II reactions must be abandoned where the formation or the decomposition of these compounds to the end products of the reaction can hardly be assumed in the light of specific peculiarities of structure and the given experimental conditions. On the other hand, there are instances where these limitations, depending upon the structural peculiarities of the reagents and the reaction products, as well as upon the different nature of the "external" factors (temperature, concentration, solvent), will not exist. In these cases the intermediate formation and the decomposition of pyrazoline derivatives may be assumed as a working hypothesis in considering the reaction mechanism, and in some cases this mechanism may even be experimentally substantiated. For instance, in the reaction of ethyl diazoacetate with the fumarate we get the ester of pyrazolinetricarboxylic acid:



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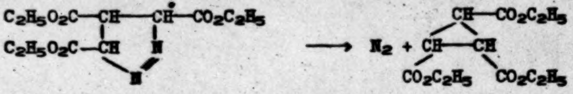
[1] The nucleophilic properties of the ethylenic linkage of vinyl acetate must, however, be less clearly marked than in simple vinyl ether, owing to resonance within the acetyl group of the vinyl acetate (cross-conjugation effect).
The superposition of the structures $CH_2 = CHOCOCH_3 \longleftrightarrow Cb_2 = CH - \overset{+}{O} = \underset{/CH_3}{C} - \bar{O}$ in contrast to the superposition of the structures

$$CH_2 = CH - OCOCH_3 \longleftrightarrow CH_2 - CH = \overset{+}{O} - COCH_3$$

which ensures the establishment of a neophilic core at the carbon atom.

which decomposes at higher temperature, liberating nitrogen and forming the ester of trimethylenecarboxylic acid.



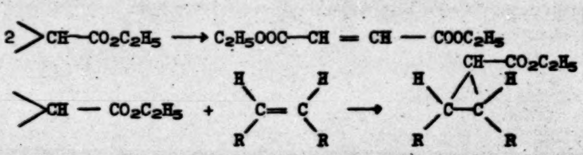
According to Loos [13], when these reagents are reacted together in the presence of powdered copper, no trimethylenecarboxylic acid is formed. When the reaction is carried out in the absence of a solvent (at 140°), the only reaction product is the fumarate. When this same reaction is carried out in ligroin, only half of the ethyl diazoacetate breaks down, liberating nitrogen, the other half yielding the pyrazolinetricarboxylic ester.

Thus the major difficulty arises in interpreting the mechanism of reactions effected in the presence of copper.

It was recalled above that the initial act of the Loos reaction seems to be the decomposition of the diazo components into an unstable "biradical" and a molecule of nitrogen

$$N_2CH{-}COOC_2H_6 \longrightarrow \;>CH{-}COC_2H_5 + N_2$$

This "biradical" either unites with itself as in the formation of the fumarate, or it attacks the doublebond in the presence of suitable ethylenic components:[1]



As we know, the question as to the existence of methylene "radicals" has been answered in the positive recently. In their thermal decomposition of diazomethane, Rice and Glasebrook [14] were the first to demonstrate the formation of free methylene, and somewhat later Pearson and his associates [15] showed that the length of the life of free methylene may change from case to case, depending on the conditions of its formation. On the basis of his own experimental research this author came to the conclusion that free methylene possesses the nature of a molecule rather than that of a radical. In the light of modern theory this conclusion should be interpreted to mean that the methylene carbon atom ($1s^2$, $2s^2$, $2p^2$) has a pair of unshared ~~atoms~~ with antiparallel spins. Pearson's conclusions apparently do not contradict the theory, since in most cases the singlet state is more stable than the triplet [16].

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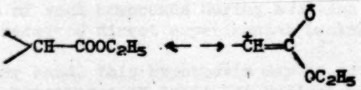
[1] The " biradical" formed here, $>CH - CO_2C_2H_5$, evidently acts upon the ethylenic linkage, as upon other additives [2], "selectively" since the double bond of the fumarate is not affected in this reaction (vide supra). Owing to the insufficiency of suitable experimental data, it is still too soon to judge whether the electrophilic properties of the fumarate double bond or still other factors play a role here.

What has been said above allows for the possible existence of radicals of molecules with bivalent carbon in Class II reactions, in the same sense as we admit now of the formation of organic ions and radicals in the course of organic reactions (vide infra).

Thus, In the Loos reaction with ethyl diazoacetate we conceive of the formation of carbethoxymethylene:

$$>CH-COOC_2H_5,$$

and it must be supposed that this radical will be more stable than methylene owing to the stabilizing influence of resonance with the carbethoxy group[1].

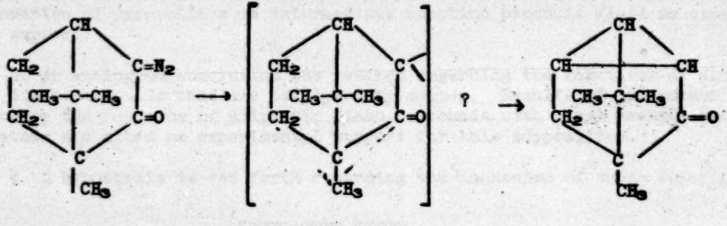


$$>CH-COOC_2H_5 \longleftrightarrow -\overset{+}{\underset{\cdot}{C}}H=C\begin{matrix}\bar{O}\\ \\ OC_2H_5\end{matrix}$$

This circumstance may be considered sufficiently explained by the fact that Class II reactions apparently are most widespread in syntheses with ethyl diazoacetate (in the Loos reactions, for example).

In syntheses with diazomethane, where products containing no nitrogen are formed as the result of its reaction with unsaturated compounds, we likewise imagine that free (or "unfree") methylenes are formed. Without this hypothesis it would be hard to explain the formation of the end products in some of the diazomethane reactions. Thus, for example, it is known that when an etheral solution of diazomethane is allowed to stand, a solid polymer, with the formula $(CH_2)x$, settles out. A few years ago, Meerwein pointed out that when an ethereal solution of diazomethane is irradiated with ultraviolet light, homologues of ethyl ether are formed alongside the solid polymer, differing from the latter in one or more methylene groups. This singular result, basically testifying to the "alkylation" of the ethyl ether by diazomethane, is hard to explain by assuming the direct action of diazomethane upon ethyl ether. The only acceptable explanation for this reaction is the assumption that the diazomethane breaks down into nitrogen and unstable, reactive methylene, which in these conditions of high dilution, immediately attacks the ether molecule.

The decomposition of diazocamphor, resulting in the synthesis of pericyclocamphor, (Bredt and Goltz), may serve as another example of the decomposition of an aliphatic diazo compound, where we imagine the formation of a group with bivalent carbon as the intermediate product of conversion:



There are still other examples of decomposition reactions of aliphatic diazo compounds, in which the formation of the end products is explained simply if we assume the formation of molecule fragments with bivalent carbon in the course of the reaction. For example, diphenylketene is formed in the decomposition of azibenzil (Curtius, Staudinger):

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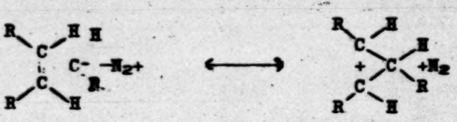
[1] In this case the resonance conditions require the antiparallel spin of the electrons in the bivalent carbon atom.

$$C_6H_5CO{-}CN_2C_6H_5 \rightarrow N_2 + (C_6H_5{-}CO{-}\underset{\wedge}{C}{-}C_6H_5) \longrightarrow (C_6H_5)_2C{=}C{=}O.$$

Inasmuch as the decomposition of the diazo component with the evolution of nitrogen is assumed in Class II reactions, it was concluded that it was possible for intermediate compounds with bivalent carbon to arise in reactions of this type. It should be remembered, however, that the hypothesis allowing for the formation of such compounds during addition reactions to ethylenic linkages has not received direct experimental backing as yet.

On the other hand, this hypothesis may be accepted in the most general form in which the hypotheses of ionic and radical mechanisms of organic reactions are assumed at the present time in dealing with the respective types of these reactions. Namely, the theory of transitional states does not provide for the appearance of free ions or radicals in the active complexes of organic reactions. However, the stabilization of these complexes is considered probable on the basis of resonance with the ionic or radical state of the respective molecule aggregates forming part of the complex, which makes it possible to conserve the classification of mechanisms according to the criteria mentioned above. It may be conjectured that the appearance of free methylenes will not serve as a criterion that is characteristic of the mechanism of Class II reactions, but this notion will retain its significance, in concealed form, in the structure of the active complex:



SUMMARY

1. The mechanism of the reactions of aliphatic diazo compounds with the olefins, resulting in the synthesis of cyclopropane derivatives or homologues of the olefins, is subjected to critical review.

2. It has been shown that in several instances of these transformations the formation of pyrazolines as intermediate reaction products finds no experimental support.

3. An analogous conclusion was reached regarding the reactions of aliphatic diazo compounds that are catalyzed by copper. Results of the author's research on the reaction of aliphatic diazo compounds with vinyl acetate and vinyl ether are cited as experimental support for this supposition.

4. A hypothesis is set forth regarding the mechanism of these reactions.

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DEHYDRATION PRODUCTS OF DIPHENYLAMINO-2-CARBOXYLIC ACIDS

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Elimination of water molecules from diphenylamino-2-carboxylic acid can be accomplished either by the direct dehydration of the acid, say with sulfuric acid, or by some other process that takes the place of dehydration, such as the conversion of the acid into the acid chloride, followed by the elimination of hydrogen chloride from the latter. Depending on the conditions under which these reactions are effected, this results in the production of different derivatives of diphenylamino-2-carboxylic acid. These transformations: those already known, new ones described in the present paper, and some others that are theoretically possible, are illustrated in the diagram below.

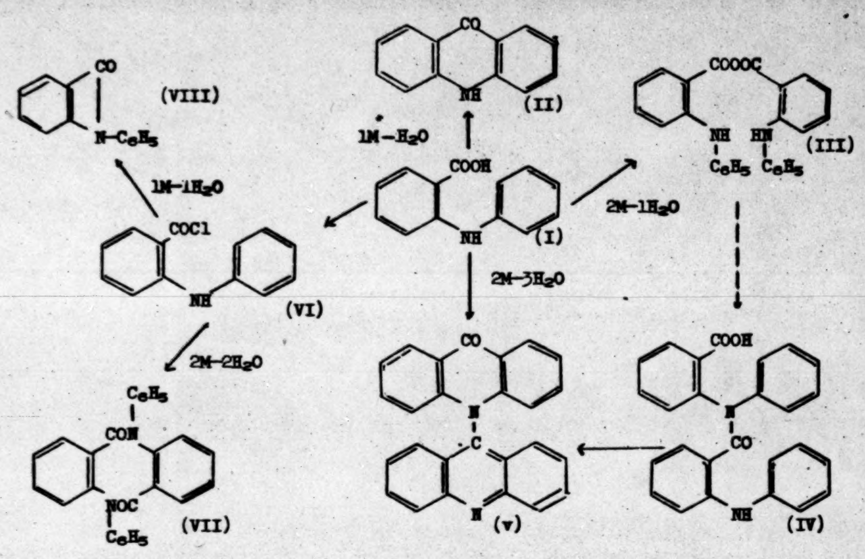
The conversion of diphenylamino-2-carboxylic acid (I) into acridone (II), cyclization, is a well-known process. Cyclization to acridone may be effected by various agents, such as sulfuric acid, acid halides, etc. Diphenylamino-2-carboxyl chloride (VI) is converted into acridone thermally, but, as described by us below, the reaction is reversed when pyridine is used to eliminate hydrogen chloride from the acid chloride.

The conversion of diphenylamino-2-carboxylic acid (I) into its acyl anhydride (III) and of (III) into N-phenyl-anthranoylo-N-phenyl-anthranilic acid (IV) have been described previously by Goodman, Arbiter, and Powell [1] as hypothetical transformations.

In the present paper we cite a number of examples to show that the conversions (I) → (III) and (III) → (IV) actually take place. A fundamental proof of the transformations (I) → (III) → (IV) was the described cyclization of the acid (IV), as the result of the further elimination of water from it by means of sulfuric acid, into a new derivative, 10,9'-acridyl-acridone (V), which we also synthesized by another method: the condensation of acridone with 9-chloroacridine.

The conversion of (I) into N,N-diphenyldianthranilide (VII) via the acid chloride (VI) is theoretically possible. It has been described by Schroter and Eisleb [2] for 2',4'-dinitrodiphenylamino-2-carboxylic acid. These authors converted this acid into its acid chloride and synthesized N,N-bis-dinitrophenyl-dianthranilide by reacting the acid chloride with pyridine. According to Anschutz [3], the chlorohydrate of anthranilic chloride is similarly converted into dianthranilide.

No one has as yet observed the transformation of diphenylamino-2-carboxylic



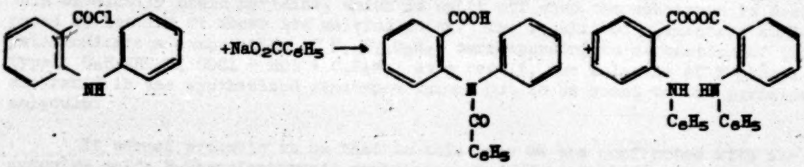
acid (I) into N-phenylanthranil (VIII), except in an intermediate state. In the present paper we describe a new compound, which may be considered to be a derivative of N-phenylanthranil (VIII).

Goodman, Arbiter, and Powell, reacting benzene sulfonyl chloride with a solution of diphenylamino-2-carboxylic acid in pyridine, obtained a yellow substance (A), m.p. 153-154°, whose properties compelled the authors to assume that this substance was the acyl anhydride of diphenylamino-2-carboxylic acid. The yellow substance (A) was transformed, by heating its solutions, into substance (B), a white acid, m.p. 201-202°. The properties of this substance could be explained by taking it to be N-phenylanthranoylo-N-phenylanthranilic acid (IV) formed by rearrangement from the acyl anhydride. In determining the molecular weights of substances (A) and (B), Goodman, Arbiter, and Powell obtained unsatisfactory results; they did not find the required proofs of the rearrangement, and, hence, summing up their observations, they did not exclude the possibility that substance (B) might be a combination of the products of dehydration of diphenylamino-2-carboxylic acid, including the unknown N-phenylanthranil, (VIII).

Letting benzene sulfonyl chloride act upon a solution of diphenylamino--2-carboxylic acid in pyridine, we obtained as the main reaction product a yellow substance that melted at 160-161° after recrystallization from acetone and whose properties indicated it to be identical with the yellow substance (A) of Goodman, Arbiter, and Powell. We also obtained a small amount of a second reaction product: N-benzoyldiphenylamino-2-carboxylic acid. The nature of the action of benzoyl chloride on diphenylamino-2-carboxylic acid was then confirmed, as usual, in tests with substituted diphenylamino-2-carboxylic acids.

To prove the structure of the dehydration products obtained in the benzoylation of diphenylamino-2-carboxylic acids, we synthesized the known acyl anhydrides of these acids by reacting the acid chlorides with the sodium salts of the respective acids. The dehydration products and the synthesized acyl anhydrides were found to be identical.

One property was found to be common to all the synthesized acyl anhydrides: upon heating, their solutions in suitable solvents are converted into acids that are proved to be isomeric by analysis. The chemical properties of these acids were found to coincide with those described by Goodman, Arbiter and Powell for substance (B). This obliged us also to assume the existence of a rearrangement of the acyl anhydrides of the diphenylamino-2-carboxylic acids into N-phenylanthranoylo-N-phenylanthranilic acids. We were able to prove that this very rearrangement occurs and is of a general nature, and that several mixed acyl anhydrides of diphenylamino-2-carboxylic acids are also subject to it. For example, much of the mixed anhydride that is formed from the acid chloride of diphenylamino-2-carboxylic acid and sodium benzoate rearranges into N-benzoyldiphenylamino-2-carboxylic acid under mild conditions, in a solution of boiling acetone. To a somewhat lesser degree this is accompanied by the disproportionation of the mixed anhydride, forming the easily identifiable acyl anhydride of diphenylamino-2-carboxylic acid:



In some analogous experiments, such as in the reaction of the acid chloride of diphenylamino-2-carboxylic acid with sodium acetate, the latter course of the reaction becomes predominant.

The disproportionation of mixed aliphatic and aliphatic-aromatic anhydrides is a well-known phenomenon, observed by Chichibabin [4] and others.

The large yield of N-benzoyldiphenylamino-2-carboxylic acid in the rearrangement of the mixed anhydride described above makes it possible to consider this process a convenient method for the synthesis of this N benzoyl acid and its relatives.

The basic evidence for the rearrangement of symmetrical anhydrides of diphenylamino-2-carboxylic acids (III) into N-phenylanthranoylo-N-phenylanthranilic acid (IV) was secured by us when cyclizing agents were allowed to act upon these acids.

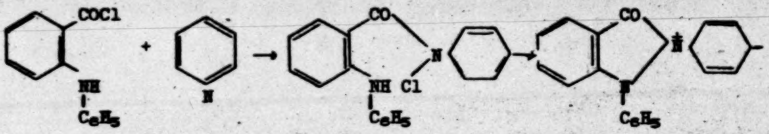
When phosphorus oxychloride acted upon the conjectured N-phenylanthranoylo-N-phenylanthranilic acid, the principal reaction product was mesochloroacridine, with a small amount of a high-melting derivative of acridine that did not dissolve in an alcoholic base (not acridone). When the same acid was reacted with concentrated sulfuric acid, the high-melting derivative of acridine was again formed, with a yield of 70%. The properties and analysis of this substance justified the assumption that it is 10,9'-acridylacridone (V), formed from (IV) by double cyclization.

Endeavors to synthesize 10,9'-acridylacridones by the condensation of 9-chloroacridines with 9-acridones in a solvent medium under mild conditions met with no success. We succeeded in effecting this reaction by fusing the input substances at high temperature without the participation of any other components. This might serve as a general method for the synthesis of substituted 10,9'-acridylacridones.

The synthesized 10,9'-acridylacridones were identical with the products of the double cyclization of N-phenylanthranoylo-N-phenylanthranilic acids.

It was of some interest to repeat the observation made by Schroter and Eisleb on the formation of substituted dianthranilide as applied to diphenylamino-2-carboxylic acid (VI → VII) Our experiments yielded an altogether unexpectedly different result. The acid chloride of diphenylamino-2-carboxylic acid was dissolved in pyridine without heating, reacting to split off hydrogen chloride. When the solution was poured off into water, a bright yellow substance separated out in a quantity that exceeded the weight of the initial acid chloride. After careful washing with water and double recrystallization from absolute alcohol the new substance melted at 136-137°. It was found to contain chemically bound pyridine, which is split off when the substance is decomposed by heating it above its melting point. The results of elementary analysis indicate a composition of $C_{18}H_{14}O_2N_2$, corresponding to a reaction of this type: $C_6H_5NHC_6H_4 \cdot COCl - HCl + C_5H_5N$; as a result, the molecule of N-phenylanthranil in the synthesized substance turned out to be bound to the pyridine molecule.

It seemed probable to us that in this case we are confronted with the ammonium amide N-phenylanthranil-pyridinium, formed as follows:



We have had to recognize the probability of such an ammonium-amide bond in some earlier instances; Decker and Schenk, for example, explain the conversion of the quaternary salt under the action of ammonia observed by them as due to the formation of such a bond [5]. This notion is not contradicted by the behavior of the new substance. The ammonium-amide bond breaks down in an aqueous acid medium, the acyl anhydride of diphenylamino-2-carboxylic acid (III) being formed with a quantitative yield as the result of hydrolysis. This last transformation corroborates the notion of the nature of the reaction involved in the well-known method for the synthesis of the acid anhydrides of acids from the acid chlorides by treating them with pyridine [6]. What doubtless happens is that the acid chloride and the pyridine react to form an intermediate compound (of the type we have now discovered), which then hydrolyzes to the acyl anhydride.

Useful contributions to this research were made by the chemist

T.A.Veselitskaya, to whom we express our deep gratitude; we also wish to thank section chief E.I.Miklashevskaya and chemists Z.T.Minayeva and O.V.Dimant for making the microanalyses.

EXPERIMENTAL

Acid Chloride of 5-Chlorodiphenylamino-2-Carboxylic Acid

8.3 g of 5-chlorodiphenylamino-2-carboxylic acid, 40 ml of toluene, and 6.6 g of phosphorus pentachloride were heated together at 50° in a flask over a water bath for 30 minutes. Then the toluene and phosphorus oxychloride were driven off in vacuo (at temperatures up to 50°), the residue in the flask crystallizing. The substance was stirred with n-pentane (10 ml), filtered out, and washed on the filter with n-pentane (10 ml). The acid chloride thus obtained was a yellow powder, that was stable in storage and had a m.p. of 100-102°. The yield was 7.5 g (85% of the theoretical).

After crystallization from n-pentane the acid chloride was obtained as yellow needles with a m.p. of 102-103°.

0.158 g substance: 0.1702 g AgCl (Carius)
Found %: Cl. 26.65
$C_{13}H_9ONCl_2$. Calculated %: Cl 26.64.

Acid Chloride of 4^4Methoxy-5-Chlorodiphenylamino-2-Carboxylic Acid

This was synthesized like the preceding compound from 7.0 g of the acid and 6.1 g of the phosphorus pentachloride in 40 ml of toluene. 7.0 g of the unrecrystallized acid chloride (an orange-yellow powder, m.p. 104-105°) was obtained (94% of the theoretical yield). The yellow needles of acid chloride fused at 110-111° after recrystallization from petroleum ether [7].

Acid Chloride of Diphenylamino-2-Carboxylic Acid (VI)

This was produced in the same manner. In this case the residue left behind in the flask after the toluene and phosphorus oxychloride had been driven off did not crystallize. When the residue was diluted with pentane a yellow solution formed, a small amount of reddish tarry substance separating out on the walls of the flask. The decanted solution was reduced in volume, upon which the acid chloride residue crystallized. The separated acid chloride, washed with pentane, was obtained as small, dark-yellow crystals, m.p. 47-50°, yield 70% of theory.

Anhydride of Diphenylamino-2-Carboxylic Acid (III)

1) Reaction of benzoyl chloride with diphenylamino-2-carboxylic acid in pyridine. To a solution of 30 g of diphenylamino-2-carboxylic acid in 90 ml of pyridine there was gradually added, with manual stirring, 21.6 g of benzoyl chloride. The solution warmed up slightly, and a deposit settled out (pyridine hydrochloride). The reaction mass was set aside to stand for 15 minutes and then poured off into 600 ml of water. Two layers were formed: oil in the bottom layer, with the top layer an aqueous one. The aqueous layer was decanted, and the oil washed with water twice. Then 100 ml of water and 50 ml of 2% acetic

acid were added to the oil. The aqueous layer was again decanted, and the oil once more washed with water, after which 80 ml of methanol was added to it with stirring. Part of the reaction product entered into solution, another part remaining undissolved as a cream-colored amorphous substance. The latter was filtered out and washed with 40 ml of boiling acetone. The substance (9 g) filtered out of the hot solution and then recrystallized from acetone (1:150) was obtained as pale-yellow prismatic crystals: m.p. 160-161°. The chemical properties of this substance agree with those described by Goodman, Arbiter, and Powell [1] for substance A, (m.p. 152-153°).

3.940 mg substance: 11.060 mg CO_2; 1.752 mg H_2O.
Found %: C 76.56; H 4.97.
$C_{26}H_{20}O_3N_2$. Calculated %: C 76.45; H 4.93.

The solution of the rest of the reaction product in methanol yielded an oil when water was added to it that gradually crystallized. After filtration the substance (14 g) pressed out on the funnel was dissolved in acetone and again separated out by the addition of water. This yielded 8 g of white crystals that melted at 165-167°. When heated in 40 ml of acetone, part of the substance dissolved; the rest dissolved when heated in a new 40-ml batch of acetone. 0.7 g of a substance with a m.p. of 190-191° settled out of the first acetone solution upon cooling; when the mother liquor was diluted with water, we obtained 5 g of a substance with a m.p. of 165-167°. 2.1 g of a substance with a m.p. of 190-191° separated out of the second batch of acetone solution when a small amount of water was added; its properties indicated that it was identical with the N-benzoyldiphenylamino-2-carboxylic acid described by us previously [8]. The substance with a m.p. of 165-167° was a mixture of diphenylamino-2-carboxylic acid and its N-benzoyl derivative.

2) Reaction of the acid chloride and the sodium salt of diphenylamino-2-carboxylic acid. To a solution of 4 g of the sodium salt of the acid in 50 ml of acetone there was added in the cold a solution of 4 g of the acid chloride in petroleum ether. A deposit soon began to settle out of the solution. Fifteen minutes later the deposit was filtered out and washed on the filter, first with acetone and then with water until there was no more chlorine ion in the wash water. The dry substance totaled 5 g in weight, or 73% of the theoretical yield, based on the salt of the acid used. When 0.5 g of the substance was crystallized from 75 ml of acetone, we got 0.37 g of pale-yellow crystals, m.p. 161-162°, which is identical with the anhydride synthesized by the benzoylation of diphenylamino-2-carboxylic acid in pyridine.

3.938 mg substance: 11.071 mg CO_2; 1.745 mg H_2O.
Found %: C 76.67, H 4.96.
$C_{26}H_{20}O_3N_2$. Calculated %: C 76.45; H 4.93.

Anhydride of 5-Chlorodiphenylamino-2-Carboxylic Acid

1) Benzoylation of the acid in pyridine. In the benzoylation test, starting with 20 g of the acid, m.p. 201-202°, in 60 ml of pyridine and 13 g of benzoyl chloride, we noted that it was outwardly similar to the benzoylation of phenylanthranilic acid described above. After the reaction product had been washed with methanol, however, only a small amount of a viscous substance, which could not be crystallized, remained insoluble. Only the input acid was recovered from the washings.

2) From the acid chloride and the sodium salt of 5-chlorodiphenylamino-2-carboxylic acid. To a solution of 7.0 g of the sodium salt of the acid in 25 ml of acetone there was added 7.0 g of the unrecrystallized acid chloride. The solution warmed up, and then a reaction product settled out. The substance was filtered out, carefully washed with methanol and water, and recrystallized (12 g) without drying from 90 ml of acetone. We obtained 7 g of the anhydride in the form of large bright-yellow needles, m.p. 124-125°. The yield was 60% of theoretical. Repeated recrystallization from acetone (1:8) did not affect the melting point of the substance.

3.552 mg substance: 8.500 mg CO_2; 1.116 mg H_2O.
Found %: C 65.26; H 3.61.
$C_{26}H_{18}O_3N_2Cl_2$. Calculated %: C 65.42; H 3.80.

Anhydride of 4'-Methoxy-5-Chlorodiphenylamino-2-Carboxylic Acid

1) Reaction of benzoyl chloride with 4'-methoxy-5-diphenylamino-2-carboxylic acid in pyridine. To a solution of 10 g of the acid (m.p. 213-214°) in 30 ml of pyridine there was added 6 g of benzoyl chloride. Fifteen minutes later the reaction mass was poured into 200 ml of water. The further treatment of the substance was identical with that described above in the effort to benzoylate phenylanthranilic acid. After the reaction product had been treated with methanol (and heating), there remained behind 2 g of an undissolved yellow substance. The substance was obtained as 1 g of yellow crystal platelets, m.p. 140-141°, after double recrystallization from acetone (1:8).

4.218 mg substance: 9.700 mg CO_2; 1.520 mg H_2O.
Found %: C 62.32; H 4.03.
$C_{28}H_{22}O_5N_2Cl_2$. Calculated %: C 62.57; H 4.12.

The substance contained in the methanol wash solution was separated out by diluting the solution with water; after double crystallization from acetone it was obtained in the form of pale yellow needles, m.p. 191-192°. This substance was found to be identical with the previously described N-benzoyl-4'-methoxy-5-chlorodiphenylamino-2-carboxylic acid, [8].

2) From the acid chloride and the sodium salt of 4'-methoxy-5-chlorodiphenylamino-2-carboxylic acid. To a solution of 7.5 g of the sodium salt of the acid in 40 ml of acetone there was added 7 g of the (commercial) acid chloride. A crystalline deposit soon began to settle out of the solution produced. One hour later the deposit was filtered out, washed on the filter with acetone and methanol, dried in air (12 g), and then recrystallized from acetone (100 ml) with the sodium chloride filtered out of the hot solution. Water was added to the warm filtrate until crystallization set in. We obtained 7.5 g of pale yellow crystals, m.p. 139-140°, in every way identical with the anhydride synthesized by the benzoylation of 4'-methoxy-5-chlorodiphenylamino-2-carboxylic acid in pyridine. The yield of the anhydride was 60% of the theoretical, based on the acid chloride employed.

N-Phenylanthranoylo-N-Phenylanthranilic Acid (IV)

2.7 g of the anhydride of phenylanthranilic acid (m.p. 160-161°) and 30 ml of 70% acetic acid were boiled together for 1 hour. Almost all the substance entered into solution during the first 20 minutes, after which a substance was observed to settle out of solution gradually. The reaction mass was diluted with 100 ml of water; the solid substance was filtered out and converted into a solution by heating with 80 ml of a 2% solution of soda. The solution was neutralized against Congo indicator by dilute hydrochloric acid. The acid that settled out was separated, washed with water, and dried (2 g). To purify it, it was dissolved in acetone (40 ml) and isolated by adding water. This reprecipitation was done twice. It resulted in the production of 1.2 g of white crystals of the acid, m.p. 202-203°, and 0.6 g of the acid, m.p. 200-201°, from the mother liquor when the latter was further diluted with water.

The acid with a m.p. of 202-203° was crystallized from methanol (1:30) as tetragonal transparent platelets, m.p. 202-203°.

4.021 mg substance: 11.310 mg CO_2; 1.760 mg H_2O.
Found %: C 76.71; H 4.90
$C_{28}H_{20}O_3N_2$. Calculated %: C 76.45; H 4.93.

When the experiment was made on a large scale (15-20 g of the anhydride), the yield of the acid with a m.p. of 200-201° was 12-16 g (80% of theory) after isolation of the crystals that settled out of the acetic acid and reprecipitating them from a soda solution.

N-Phenyl-p-Chloroanthranoylo-N-Phenyl-p-Anthranilic Acid

3 g of the anhydride of 5-chlorodiphenylamino-2-carboxylic acid and 30 ml of glacial acetic acid were heated until the acid boiled gently for 1 hour. A red solution was formed, which grew somewhat paler toward the end of heating. The solution was poured off into 100 ml of water. The deposited substance was filtered out, washed with water, and converted into a solution of the sodium salt by heating to boiling with 300 ml of a 5% solution of soda. The acid was precipitated from the solution by dilute hydrochloric acid. The washed and dried acid was obtained as 2.7 g (90%) of an amorphous cream-colored powder. The precipitated acid is soluble in exceedingly small volumes of acetone, methanol, ethyl alcohol, and toluene. When such solutions are allowed to stand, most of the acid (80%) settles out of toluene. Repeated crystallization of the substance from toluene then requires much more solvent (1:25) and boiling. The crystals of the acid obtained from toluene had a m.p. of 185-186°. The substance was obtained with the same melting point after supplementary crystallization from 80% methanol (1:60), from which the acid settled out as pale cream-colored prisms.

4.292 mg substance: 10.317 mg CO_2; 1.489 mg H_2O.
Found %: C 65.55; H 3.88.
$C_{28}H_{18}O_3N_2Cl_2$. Calculated %: C 65.42; H 3.80.

It was difficult to determine the melting point for samples of the acid that had been recrystallized repeatedly from toluene, since at the temperature of 185-190° it was converted into high-boiling chloroacridone as soon as the substance began to grow moist. Such samples of the acid were converted into solutions of the sodium salt, from which the acid was precipitated by dilute hydrochloric acid. The precipitated acid again dissolved easily in organic solvents, and the observation described above was repeated when further recrystallizations were made.

The easy initial solubility of the precipitated acid (B) was noted in the observations of Goodman, Arbiter and Powell; they attributed this phenomenon to hydration. Our experiments confirmed this explanation.

N-4'-Methoxyphenyl-4-Chloroanthranoylo-N-4'-Methoxyphenyl-4-Chloroanthranilic Acid

The rearrangement of the anhydride of 4'-methoxy-5-chlorodiphenylamino--2-carboxylic acid was effected under the same conditions as those described above, with the same yield of the reaction product. The acid was recrystallized from toluene in the form of small yellow needles, m.p. 187-188°. The sodium salt of this acid is less soluble in a boiling weak solution of soda than the same salt of the preceding acid.

Rearrangement of the Mixed Anhydrides of Benzoic Acid and Diphenylamino-2-Carboxylic Acid

To a suspension of 1.2 g of dehydrated sodium benzoate in 10 ml of acetone 2 g of the acid chloride of diphenylamino-2-carboxylic acid was added. There were no signs of immediate reaction. The mixture was heated over a water bath until the acetone boiled and was gradually driven off, the process taking about 20 minutes. The precipitated suspension of sodium benzoate gradually disappeared as this was done. Water (20 ml) was added to the reaction mass, which had thus been reduced to the volume of a few milliliters; the oil that separated out soon hardened. The solid substance was filtered out and washed on the filter with water and then with acetone (5 ml). The 2 g of solid substance thus obtained was treated with a warm 2.5% solution of sodium bicarbonate (400 ml). The part of the substance that did not dissolve (0.4 g) was dissolved upon heating in 50 ml of acetone; upon cooling 0.25 g of crystals of the anhydride of diphenylamino-2-carboxylic acid, with a m.p. of 156-158°, settled out.

The bicarbonate solution was precipitated with dilute hydrochloric acid. The white acid that settled out was filtered out, washed, dried, and identified as N-benzoyl-diphenylamino-2-carboxylic acid, m.p. 190-191°. Its experimental yield was equivalent to 42% of the theoretical yield, based on the sodium benzoate used.

10,9'-Acridylacridone

10 g of N-phenylanthranoylo-N-phenylanthranilic acid (m.p. 200-201°) and 125 ml of concentrated sulfuric acid were heated together for 1.5 hours over a boiling water bath. When heating began a dark red solution was formed, which grew much lighter later. The reaction solution was poured into 1.5 liters of water. The substance that settled out was filtered out and carefully washed, first with water and then with acetone. The residue (dry weight 7 g) was dissolved in 150 ml of boiling pyridine. The yellow crystals that settled out of solution upon standing (4 g) were separated and again recrystallized from 100 ml of boiling pyridine. After this repeated crystallization we obtained 3 g of light yellow crystals with a m.p. of 383-384°. The substance sublimes slightly during fusion; it is insoluble in alcoholized bases, nor does it change when heated with the latter; it does not dissolve in water or alcoholic hydrochloric acid (it turns red, becoming yellow again when diluted with water).

4.115 mg substance; 12.664 mg CO_2; 1.619 mg H_2O.
6.399 mg substance: 0.434 ml N_2 (18°, 738.5 mm).
Found %: C 83.92; H 4.40; N 7.73.
$C_{28}H_{16}ON_2$. Calculated %: C 83.85; H 4.33; N 7.52.

After the mother liquor had been diluted with water the pyridine was steam-distilled off. The residue was an emulsion of the substance in water. The emulsion was broken down by acidulating it with hydrochloric acid. The separated solid substance (5.5 g) was treated with an alcoholic base. 0.5 g of acridone was isolated from the alcohol-alkali filtrate. The substance that did not dissolve in the alcoholic base was acridylacridone; its yield in this experiment was 70% of the theoretical.

Another similar experiment was set up, in which the substance produced in the reaction (8 g) – before it was recrystallized from pyridine – was treated with an alcoholic base during heating in order to resolve the question of where the acridone is formed in the experiment. In this case, too, acridone (0.2 g) was isolated from the alcoholic filtrate. On the other hand, the pure acridylacridone was dissolved in pyridine and the solution subjected to steam distillation. This recovered the acridylacridone unchanged, without a trace of acridone, which indicates that the trace of acridone found originated during the process of cyclization, and not as a result of the cleavage of the acridylacridone.

Our subsequent endeavors to cleave the acridylacridone at the 10,9' bond by boiling it with an alcoholic base, heating it with phosphorus oxychloride, or converting it into the chloromethylate and subsequently heating it with an alkali, met with no success.

Synthesis of 10,9'-Acridylacridone from Acridone and 9-Chloroacridine

A mixture of equal amounts of acridone and 9-chloroacridine was fused by heating it for 30 minutes, gradually raising the temperature to 300°. During subsequent heating, the melt was treated with an alcoholic base, then with alcohol, water, and acetone. The substance that remained insoluble, with a dry weight of 0.55 g, was obtained after recrystallization from 15 ml of pyridine as 0.35 g of the flat hexahedral, light-yellow crystals characteristic of acridylacridone with all the properties of acridylacridone.

3.592 mg substance: 11.050 mg CO_2; 1.399 mg H_2O.
4.424 mg substance: 0.296 ml N_2 (21°, 745.6 mm).
Found %: C 83.89; H 4.36; N 7.61.
$C_{28}H_{16}ON_2$. Calculated %: C 83.85; H 4.33; N 7.52.

3-3'-Dichloro-10,9'-Acridylacridone

3 g of N-phenyl-p-chloroanthranoylo-N-phenyl-p-chloroanthranilic acid and 30 ml of concentrated sulfuric acid were heated for 1.5 hours over a boiling water bath. The solution formed was poured into water, and the precipitate that settled out was filtered out, and carefully washed with water and then with acetone. This yielded 2.5 g of an orange-yellow cyclization product; the latter was dissolved in 40 ml of boiling pyridine. The crystals that settled out upon cooling: pale yellow needles, were separated out and washed with acetone; they weighed 1.1 g. For analysis the substance was further washed with an alcoholic base, alcohol, water, and acetone, and again recrystallized from pyridine (1:20).

The dichloroacridylacridone obtained was in the form of light-yellow needles with a m.p. of 327-330°, resembling unsubstituted acridylacridone in its properties.

4.075 mg substance: 10.548 mg CO_2; 1.321 mg H_2O.
Found %: C 70.60; H 3.62.
$C_{26}H_{14}ON_2Cl_2$. Calculated %: C 70.76; H 3.20.

Synthesis of 3,3'-Dichloro-10,9'-Acridylacridone from 3-Chloroacridone and 6,9-Dichloroacridine

A mixture of 0.45 g of 3 chloroacridone and 0.5 g of 6,9-dichloroacridine was fused, and the melt obtained was treated with the same reagents as were used in the experiment for the synthesis of 10,9'-acridylacridone. We obtained 0.35 g of the dichloroacridylacridone: after recrystallization from pyridine the substance was prepared in the shape of pale yellow needles, m.p. 327-330°, identical with what was synthesized by cyclization.

3.280 mg substance: 8.519 mg CO_2; 0.998 mg H_2O.
Found %: C 70.83; H 3.40.
$C_{26}H_{14}ON_2Cl_2$. Calculated %: C 70.76; H 3.20.

1,1,2'-(N-Phenylanthranil)-Pyridinium

1.5 g of the acid chloride of diphenylamino-2 carboxylic acid (VI) was poured in the cold into 40 ml of pyridine. Most of the acid chloride entered solution at once, the remainder did so after the residue was rubbed with a stick. The solution was diluted with 120 ml of water. The bright yellow deposit that settled was filtered out and washed on the filter, first with water and then with alcohol; its air-dry weight was 1.7 g. After triple rerecrystallization from absolute ethyl alcohol (1: 15), the substance was obtained as yellow crystals, m.p. 136-137°.

3.355 mg substance: 9.704 mg CO_2; 1.607 mg H_2O.
5.278 mg substance: 0.471 ml N_2 (20°, 717 mm).
Found %: C 78.88; H 5.35; N 9.83.
$C_{18}H_{14}ON_2$. Calculated %: C 78.90; H 5.14; N 10.21.

At a temperature of about 180° (N-phenylanthranil)-pyridinium (IX) decomposed, yielding pyridine; the decomposition residue dissolves in pyridine, but this does not result in the reconstitution of the original substance. When (IX) is boiled in water the odor of pyridine is noticed. When (IX) is boiled in water that has been acidulated with acetic acid, the acyl anhydride (III) is formed quantitatively. When it is boiled in a weakly alkaline alcoholic medium, (IX) is stable, though it breaks down in a medium acidulated with a mineral acid. When (IX) is heated for 15 minutes with concentrated sulfuric acid, acridone and phenylanthranilic acid are formed.

SUMMARY

1. Examples of a new reaction, the rearrangement of the acyl anhydrides of diphenylamino-2-carboxylic acids, are described.

2. The fundamental difference in the action of sulfuric acid and of phosphorus oxychloride during the cyclization of N-aroyldiphenylamino-2-carboxylic acid is shown.

3. The product of the reaction between the acid chloride of diphenylamino-2-carboxylic acid and pyridine, which is assumed to be 1,1',2'-(N-phenylanthranil)-pyridinium was isolated, its formation and properties confirming the existence of intermediate products during the synthesis of the anhydrides of acids from their acid chlorides in a pyridine medium.

4. New compounds are described: the acyl anhydrides of diphenylamino-2-carboxylic acids, N-phenylanthranoylo-N-phenylanthranilic acid, and 10,9'-acridylacridone.

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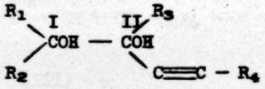
RESEARCH ON TRANSFORMATIONS OF THE PINACOLS WITH SUBSTITUTED ACETYLENE RADICALS

VI. SYNTHESIS AND TRANSFORMATION OF METHYLDIPHENYL-PHENYLACETYLENYLETHYLENE GLYCOL (SYMM.) [1] (2,3,5-TRIPHENYLPENTYNE-4-DIOL-2,3).

E. D. Venus-Danilova and L. A. Pavlova

Organic Chemistry Laboratory of the Leningrad Technological Institute named after the Leningrad Soviet

In studying the transformations of pinacols with substituted acetylene radicals of the general type (I)



(I)

when sulfuric acid was used as a catalyst, it was found that when dimethylphenyl phenyl-acetylenylethylene glycol [2] [(I): R_1 and $R_2 = CH_3$, R_3 and $R_4 = C_6H_5$] is heated with 30% (by weight) of sulfuric acid, it is isomerized to a substituted hydroxy-dihydrofuran – the product of the cyclization of an unsaturated γ-ketone alcohol, formed from the pinacol by an acetylene-allene rearrangement.

Likewise, only the corresponding substituted hydroxyhydrofuran was isolated for dimethyl-p-tolylphenylacetylenylethylene glycol [3] [(I): R_1 and $R_2 = CH_3$, $R_3 = C_6H_4CH_3$, $R_4 = C_6H_5$].

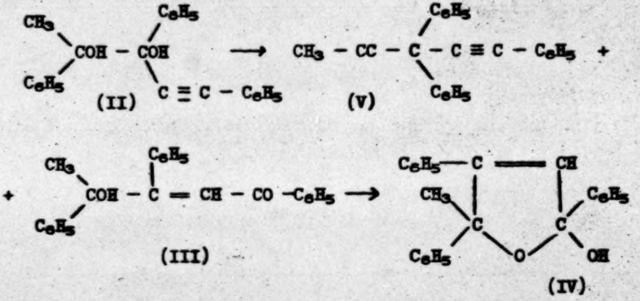
In studying the products of the transformation of dimethylphenyl-tert.-butylacetylenylethylene glycol [(I). R_1 and $R_2 = CH_3$, $R_3 = C_6H_5$, $R_4 = C(CH_3)_3$], we were able to find – in addition to the end product of the transformation – a substituted hydroxydihydrofuran and an unsaturated γ-ketone alcohol, and to show the mutual conversions of these two substitutions [4].

A glycol with two phenyl groups attached to the first hydroxylated carbon atom – diphenylmethylphenylacetylenylethylene glycol [1] [(I): R_1, R_2, and $R_4 = C_6H_5$, $R_3 = CH_3$] differs from the pinacols cited above in that, under the conditions we ordinarily used in studying the transformations of the pinacols (30% sulfuric acid and heating), it suffered no change, being dehydrated to a ketone of the acetylene series – methylphenyl-phenylacetylenylbenzoylmethyl — only upon heating to gentle boiling with 40% sulfuric acid.

The subject of the present investigation was a pinacol that is an isomer of asymm. diphenylmethylphenylacetylenylethylene glycol (1,1,4-triphenyl-2-methylbutyne-3-diol-1,2), with methyl and phenyl groups attached to the first hydroxylated carbon atom [(I): R_1, R_3 and R_4 = C_6H_5, R_2 = CH_3] – symm. methyldiphenyl-phenylacetylenylethylene glycol (2,3,5-triphenyl-pentyne-4-diol-2,3).

Investigation of the products of transformation of this pinacol demonstrated that, together with an unsaturated γ-ketone alcohol (III) and a small quantity of a substituted hydroxydihydrofuran (IV), there is also formed a ketone of the acetylene series (3,3,5-triphenylpentyne-4-one-2) (V) with a yield of some 37% of theory (for 30% acid).

Hence, in this case there take place both acetylene-allene and pinacolin rearrangements of the pinacol:

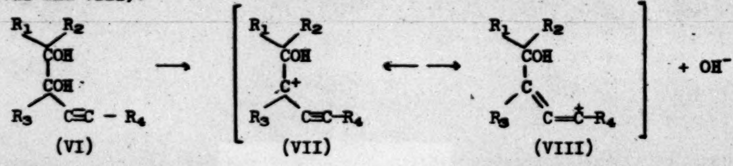


The structure of the transformation products obtained indicates that in the symm. methyldiphenyl-phenylacetylenyl-ethylene glycol, as in all the pinacols of this group investigated earlier the hydroxyl located in the alpha position at the triple bond is mobile.

As has already been noted, a similar observation was made for pinacols with acetylene and vinylacetylene radicals [5].

Three of the pinacols investigated by us [(I): R_1 and R_2 = CH_3] undergo acetylene-allene rearrangement when exposed to sulfuric acid. When all the aliphatic radicals were replaced by aromatic ones (R_1 and R_2 = C_6H_5), the pinacolin rearrangement was a fundamental kind of transformation; partial substitution of aromatic radicals (R_1 = CH_3, R_2 = C_6H_5) for the aliphatic ones made it possible to observe both types of transformation in a single pinacol.

The results obtained enable us to set down the general scheme of transformations of the group of pinacols under investigation. Two mesomeric structures (VII and VIII):



are possible for the organic cation produced as the result of the elimination of the mobile hydroxyl group from the pinacol (VI) by the action of sulfuric acid.

The neutralization of the positive charge on the organic cation may be effected either by the addition of a hydroxyl ion or by the migration of one of the radicals with its electron pair from the adjacent carbon atom, and the subsequent stabilization of the reconstituted organic cation by transfer of a proton to the solution.

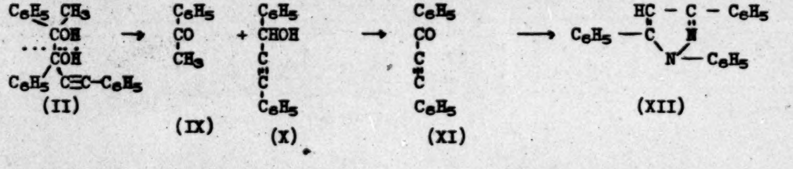
The fact that the transformation products obtained are either ketones of the acetylene series or unsaturated γ-ketone alcohols indicates that the structure (VII) is stabilized by the migration of a radical with ensuing changes, whereas the structure (VIII) is stabilized by the addition of a hydroxyl group.

The end product of the rearrangement depends on the nature of the radicals R_1, R_2, R_3, and R_4. As our research has demonstrated, migration of the phenyl group occurs more easily than that of the methyl group, which may be due to the different nature of the CH_3 and C_6H_5 radicals. In the R_3 position, phenyl apparently facilitates the acetylene-allene rearrangement, as it results in a compound containing a chain with conjugated double bonds (an unsaturated γ-ketone alcohol). Even when $R_3 = CH_3$, however, an acetylene-allene rearrangement is possible, as was proved by our preliminary experiments on the products of the transformation of trimethylphenylacetylenyl-ethylene glycol [(I): R_1,R_2 and $R_3 = CH_3$, $R_4 = C_6H_5$].

The nature of the R_4 radical apparently exerts no direct effect upon the nature of the pinacol transformation, but makes itself felt in the cyclization of the unsaturated γ-ketone alcohol to a substituted hydroxydihydrofuran. Our experiments established that when $R_4 = C_6H_5$ (R_1 and $R_2 = CH_3$), the unsaturated γ-ketone alcohol is completely converted into a substituted hydroxydihydrofuran [2,5], whereas when $R_4 = C(CH_3)_3$, R_1, R_2, and R_3 remaining the same, the cyclization of the unsaturated γ-ketone alcohol is only partial. We are able to isolate both ring and chain isomers in this reaction [4]. It may be predicted that the products of transformation of a pinacol that differs from the one described in this paper solely in the presence of a tertiary butyl radical at the R_4 position will include both an acetylene ketone and an unsaturated γ-ketone alcohol, besides an even smaller quantity of the substituted hydroxydihydrofuran.

We synthesized symm. methyldiphenyl-phenylacetylenylethylene glycol (II) by the ordinary Iotsich method from phenylacetylenemagnesium bromide and methylbenzoin.

Endeavors to effect the crystallization of the thick oil produced were unsuccessful; upon vacuum distillation the thick caramellike substance underwent thermal decomposition into acetophenone (IX) and phenyl-phenylacetylenylcarbinol (X):



The presence of acetophenone was proved by production of the semicarbazone. The phenyl-phenylacetylenylcarbinol (m.p. 49-50°) was oxidized by chromic anhydride [6] to phenyl-phenylacetylenyl ketone (XI) (m.p. 51-52°), which yielded 1,3,5-triphenylpyrazole (XII) (m.p. 137-138°) upon condensation with phenylhydrazin [7].

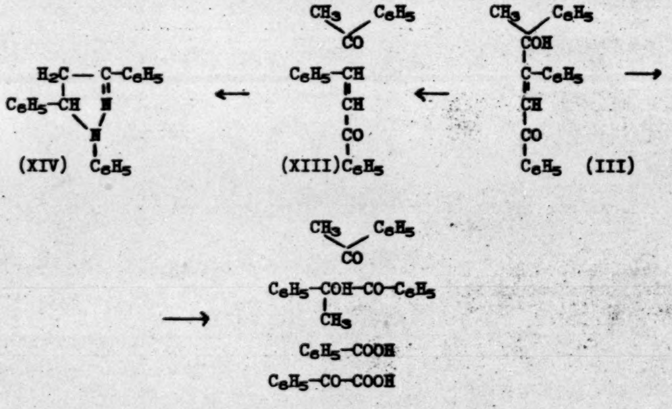
Similar ketonic cleavages have been observed by several chemists for various aliphatic-aromatic and aromatic pinacols [8].

The symm. methyldiphenyl-phenylacetylenylethylene glycol was purified by repeated washings with hot water, with vigorous stirring and subsequent extraction with ether. After elimination of the ether, the pinacol was a transparent, almost glasslike mass, which softened at 36-38°. Determination of the molecular weight, elementary analysis, and cleavage by potash [9] all confirmed the structure of the pinacol.

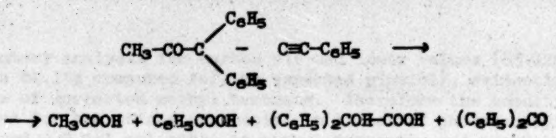
The pinacol was subjected to the action of 20%, 30%, and 40% sulfuric acid, with gentle boiling and vigorous stirring, for 3 hours.

In the first instance, the principal transformation product was an unsaturated γ-ketone alcohol – 2,3,5-triphenylpenten-3-ol-2-one-5 (III), with an admixture of about 10% of an acetylenic ketone – diphenyl-phenylacetylenylacetylmethane (3,3,5-triphenylpentyn-4-one-2) (V); m.p. 96-97°; semicarbazone m.p. 109°.

The structure of the γ-ketone alcohol was proved by oxidizing it to acetophenone, methyl benzoate, and benzoic and benzoylformic acids. Moreover, the ketone alcohol, like the pinacol, is cleaved in vacuo into acetophenone and benzalacetophenone (XIII) (m.p. 55-56°), which is converted into 1,3,5-triphenylpyrazoline when heated with phenylhydrazine [10]. Some of the α-ethylenic alcohols decompose in a similar manner [11].



The structural formula of the ketone was established from its oxidation products – acetic, benzoic and benzilic acids and benzophenone:



$$CH_3-CO-\underset{C_6H_5}{\overset{C_6H_5}{C}} - C\equiv C-C_6H_5 \longrightarrow$$

$$\longrightarrow CH_3COOH + C_6H_5COOH + (C_6H_5)_2COH-COOH + (C_6H_5)_2CO$$

(V)

The weak fluorescence of the acid solution remaining behind after the γ-ketone alcohol had been separated from the ketone indicated the presence of traces of a substituted hydroxydihydrofuran, but only a negligible quantity of the latter substance was isolated upon neutralization.

With 30% sulfuric acid the yield of the acetylenic ketone rose to 37%. In this experiment we obtained, in addition to the unsaturated γ-ketone alcohol, a substituted hydroxydihydrofuran – 2,4,5-triphenyl-5-methyl-2-hydroxydihydrofuran-2,5 (IV) (m.p. 125-127°) with a yield of about 15% after neutralizing the strongly fluorescent acid solution. This substance forms a ketal and complex salts with platinum chloride (m.p. 171-173°) and auric chloride (m.p. 174-176°).

The action of 40% sulfuric acid upon the pinacol yielded the same products, but the yield of the ketone now rose to 47% and that of the substituted hydroxydihydrofuran to 18.5%, while the amount of unsaturated γ-ketone alcohol decreased.

We used the example of dimethylphenyl-tertiary-butyl-acetylenylethylene glycol to prove that the unsaturated γ-ketone alcohol can be cyclized to a substituted hydroxydihydrofuran by the action of sulfuric acid. And in this case as well we were able to convert part of the oily product, corresponding to a γ-ketone alcohol, into a substituted hydroxydihydrofuran (yield 33%). This again confirmed the assertion that the liquid product of the pinacol transformation is an unsaturated γ-ketone alcohol.

EXPERIMENTAL

I. Synthesis of Methyldiphenyl-phenylacetylenylethylene Glycol – 2,3,5-Triphenylpentyne-4-diol-2,3 (II)

The initial substances for the glycol synthesis were methyl benzoate (m.p. 65-66°) and phenylacetylene (b.p. 140-141°).

An ether solution of methyl benzoate, taken in theoretical quantity, was added to a freshly prepared solution of phenylacetylenemagnesium bromide. As the methyl benzoate was added, the grayish color of the reaction mass disappeared; after all the methyl benzoate had been added, the solution was dark yellow, with a slight white deposit.

Twenty four hours later the reaction mass was decomposed with water, acidulated with dilute sulfuric acid, and extracted with ether. The ether extract was washed with a solution of soda and dried with sodium sulfate. After the ether was driven off, we got a viscous yellow substance, which did not crystallize in spite of all the steps taken to cause it to do so. After the excess phenylacetylene was driven off in vacuo (b.p 34° at 11 mm, and a bath temperature of 58°), the product was recovered as a slightly softening solid mass.

Elementary analysis for carbon yielded lower values (83.12% of carbon instead of the 84.15% computed for the expected pinacol), evidently because of the traces of unreacted methyl benzoate. Therefore the conditions were slightly changed for the second synthesis: an excess of phenylacetylenemagnesium bromide was used – 2.5:1 mol ratio to methyl benzoate, and not 2:1 as in the first test; moreover, the reaction mass was warmed up for 3 days, to keep the ether gently boiling. After decomposition and the driving off of the ether, the excess phenylacetylene was carefully driven off in vacuum; the residue of phenylacetylene left behind was eliminated from the viscous mass by repeated washings with hot water and vigorous stirring. Then the ether extract was made and dried for a long time with sodium sulfate. After the ether had been removed the caramellike yellow mass, which softened at 36-38°, was analyzed.

0.1090 g substance: 0.3374 g CO_2; 0.0603 g H_2O.
0.1001 g substance: 0.3094 g CO_2; 0.0569 g H_2O.
0.3866 g substance: 22.39 g C_6H_6: Δt 0.37°.
Found %: C 84.30,84.29; H 6.32,6.23; $\underline{M}$ 333.
$C_{23}H_{20}O_2$. Calculated %: C 84.15; H 6.09 ; $\underline{M}$ 328.

Determination of hydroxyl groups by the Zerewitnoff method as modified by Terentyev:

0.0569 g substance: 8.2 ml CH_4(19°, 764 mm).
Found %: v_0 7.55; OH 13.26.
$C_{23}H_{18}(OH)_2$. Calculated %: v_0 7.75; OH 13.66.

When the pinacol was cleaved by potassium carbonate at 280°[9], an acetylenic hydrocarbon was found in precipitating a deposit with ammoniacal silver nitrate.

Ketonic Cleavage of the Pinacol (II)

When an endeavor is made to distill the pinacol *in vacuo* it is cleaved. The following fractions were collected:

1. B.p. 85°, pressure 1.5 mm (bath temp. 200°);
2. B.p. 120-170°, pressure 1.5 mm (bath temp. 214°);
3. B.p. 170-175°, pressure 1 mm (bath temp. 202°).

The first fraction has the strong odor of acetophenone and quantitatively yields the semicarbazone with a m.p. of 200-201°, which exhibits no depression of the melting point when mixed with the known semicarbazone of acetophenone.

The second and third fractions were redistilled in vacuum. The first fraction again yielded acetophenone with a b.p. of 63° at 5 mm; the second fraction had a b.p. of 178-181° at 3 mm; and the third fraction had a b.p. of 181-183° at 4 mm. The latter two hardened upon distillation into crystals with a m.p. of 49-50°.

Analysis of Substance with 49-50° m.p.

0.1090 g substance: 0.3448 g CO_2; 0.0580 g H_2O.
0.0966 g substance: 0.3061 g CO_2; 0.0544 g H_2O.
0.2648 g substance: 15.45 g C_6H_6; Δt 0.41°.
Found %: C 86.27, 86.42; H 5.91, 6.25; $\underline{M}$ 209.
$C_{15}H_{12}O$. Calculated %: C 86.53; H 5.70; $\underline{M}$ 208.

The above data correspond to phenyl-phenylacetylenyl-carbinol (X).

In the literature [12] this substance is described as a colorless oil with a b.p. of 207-208° at 13 mm.

To confirm the structure of the alcohol produced, which was a crystalline product in contrast to the literature data, the substance was oxidized by chromic anhydride to acetic acid.

Oxidation of the Substance with a m.p. of 49-50° (X) [6]. To a solution of 0.9 g of the alcohol in 8 ml of glacial acetic acid 0.3 g of chromic anhydride was added. The mixture was shaken up for 2 hours at room temperature, and then heated over a water bath for 1 hour. An ether extract was made of the green solution obtained; after washing with a soda solution and with water, the extract was dried with sodium sulfate. After the ether had been driven off, we obtained a rapidly crystallizing oil. The crystals were purified in a porous dish; they then melted at 51-52°. The substance produced a depression of the melting point when mixed with the initial alcohol and did not exhibit the qualitative reaction for a hydroxyl group.

The substance thus obtained was heated with a few drops of phenylhydrazine for 6 hours over a water bath. The yellow mass that separated out melted at 137-138° after recrystallization from ether.

It is known from the literature that reacting benzoylphenylacetylene (XI) with phenylhydrazine yields 1,3,5-triphenylpyrazole (XII) with a m.p. of 139.5° [7].

Thus, analysis of the cleavage product of the pinacol, oxidation of this cleavage product, and phenylhydrazine condensation of the unsaturated ketone obtained as the result of oxidation all confirm that the substance with a m.p. of 49-50° is phenyl-phenylacetylenylcarbinol, while the latter, in turn, is proof that the pinacol we synthesized has the structure of methyldiphenyl-phenylacetylenylethylene glycol (II).

II. Action of Sulfuric Acid Upon Methyldiphenyl-phenylacetylenylethylene Glycol

In view of the fact that the diphenylmethylphenylacetylenylethylene glycol (asymm.) previously studied by us [1], which is isomeric with methyldiphenylphenylacetylenylethylene glycol (symm.), was changed only when acted upon by 40% sulfuric acid, we commenced an investigation of the transformation of the symm. glycol when acted upon by sulfuric acid in the same concentration.

Experiment 1. Action of 40% Sulfuric Acid on the Pinacol

To 13.5 g of the pinacol there was added 10 times the quantity of sulfuric acid, and the mixture was heated to boiling, with vigorous stirring. The top layer darkened, while the bottom layer took on an orange-green hue and fluoresced strongly. An ether extract of the acid solution yielded 10 g of an oily product, from which a crystalline substance separated out upon standing. The addition of alcohol aided in the separation of the crystals, which are insoluble in cold alcohol. The substance melted at 96-97° after recrystallization from boiling alcohol. No more crystals settled out of the oily liquid after the alcohol had been driven off.

The strongly fluorescent acid solution was neutralized with soda after the crystalline and oily substances had been separated out; this caused the fluorescence and color to vanish, and a solid reddish substance to separate out; this substance was purified very easily by washing with a small amount of a mixture of ether and petroleum ether in a porous dish, followed by recrystallization from the same mixture by boiling it with a small amount of activated charcoal. The substance was isolated as small crystals with a m.p. of 125-127°.

Investigation of the Crystalline Substance with a m.p. of 96-97° (V)

The substance is insoluble in cold alcohol or petroleum ether, the solubility increasing with heating; it has no hydroxyl group and gradually yields semicarbazone that melts at 109° after recrystallization from alcohol.

Analysis of Substance with 96-97° m.p.

0.1016 g substance: 0.3327 g CO_2; 0.0562 g H_2O.
0.1139 g substance: 0.3729 g CO_2; 0.0622 g H_2O.
0.2795 g substance: 13.42 g C_6H_6: Δt 0.36°.
Found %: C 89.31, 89.39; H 6.14, 6.06; M 300.
$C_{23}H_{18}O$. Calculated %: C 89.03; H 5.81; M 310.

Analysis of Semicarbazone with 109° m.p.

0.1030 g substance; 0.2952 g CO_2; 0.0546 g H_2O.
0.1221 g substance: 12.4 ml N_2 (18°, 750 mm).
0.1215 g substance; 11.9 ml N_2 (16.5°, 761 mm).
Found %: C 78.16; H 5.88; N 11.51, 11.36.
$C_{24}H_{21}ON_3$. Calculated %: C 78.47; H 5.72; N 11.45.

The analysis data indicate that the substance with a m.p. of 96-97° is a ketone. The yield of the ketone was 6 g, corresponding to 47% of theory.

By dehydrating the methyldiphenyl-phenylacetylenylethylene glycol we can produce one of three isomeric ketones of the same structure as in the dehydration of diphenylmethylphenylacetylenylethylene glycol [1]. The presence of methylphenyl-phenylacetylenylbenzoylmethane (m.p. 100-101°) is impossible in this case, since the ketone with a m.p. of 96-97° isolated by us produced a sharp depression of the melting point when mixed with the methylphenyl-phenylacetylenylbenzoylmethane that we synthesized by dehydrating asymm. diphenylmethylphenylacetylenylethylene glycol [1]. Hence, the structure of the ketone synthesized by us in this experiment must be either that of diphenyl-phenylacetylenylacetylmethane (3,3,5-triphenylpentyn-4-one-2) or 1,5,5-triphenylpentyn-1-one-3.

The ketone was oxidized by an aqueous pyridine solution of potassium permanganate in order to establish its structure.

Oxidation of the ketone with a m.p. of 96-97°. This was done by heating 4.2 g of the ketone in 80 ml of pyridine to 40° with a solution of potassium permanganate (3.5 g of the salt in 150 ml of water). The reaction set in fairly quickly; 2 hours after oxidation was begun, the remaining 2.2 g of dry potassium permanganate salt was added in small portions during the course of 3 hours. The reaction mass was stirred for another 4 hours, being heated to 40-50° during the last hour. The aqueous pyridine layer became colorless upon standing.

The manganese dioxide was filtered out and washed with a small quantity of hot water to separate the neutral products of oxidation. Treating the manganese dioxide with ether yielded 0.6 g of a solid substance with a m.p. of 96-97°, which corresponded to the initial ketone and caused no depression of the melting point when mixed with the latter.

The volatile neutral products were driven off with steam from the filtrate and the wash waters, the pyridine and part of the water being eliminated by heating over a boiling water bath with slight vacuum. The calculated quantity of dilute sulfuric acid was chemically bound while the pyridine was driven off, and then the neutral substances were extracted with ether. After the ether had been driven off there remained 0.3 g of a substance with a m.p. of 46-47° that caused no depression of the melting point when mixed with benzophenone. The corresponding semicarbazone fused at 165-166° and caused no depression of the melting point when mixed with a known sample of the semicarbazone of benzophenone.

The neutral products that did not distill off with steam were extracted with ether from the residue after the volatiles had been driven off; they yielded another 1.1 g of benzophenone, which was likewise identified by its melting point and by its corresponding semicarbazone.

After the neutral substances (benzophenone) had been eliminated, the salts of the organic acids were concentrated over a water bath. When dilute sulfuric acid was added to effect decomposition, the odor of acetic acid was noticed and a light deposit separated out; this deposit fused at 119-120° after recrystallization from water, drying, and sublimination, and caused no depression of the melting point when mixed with benzoic acid.

The acids, dissolved in water, were driven off by boiling with freshly prepared silver carbonate to produce the silver salts of the organic acids. The salts produced were stable and did not decompose upon heating and recrystallization.

Analysis indicated that the salt was silver acetate.

0.1619 g salt : 0.1064 g Ag.
0.1044 g salt : 0.0989 g Ag.
Found %: Ag 64.48, 64.56.
CH_3COOAg. Calculated %: Ag 64.65.

The organic acids that were not volatile with steam and remained behind after the acetic acid had been driven off were extracted with ether; after the ether had been driven off, 0.1 g of these acids was obtained in the solid state, with a m.p. of 149-150° after refining in a porous dish. The acid caused no depression of the boiling point when mixed with benzilic acid and yielded the bright-red color with strong sulfuric acid that is characteristic of benzilic acid.

Thus, the ketone oxidation products obtained – acetic, benzoic, and benzilic acids, as well as benzophenone, the product of the further oxidation of benzilic acid – justify the assertion that our pinacol ketone is diphenyl-

-phenylacetylenylacetylmethane – 3,3,5-triphenylpentyn-4-one-2 (V).

The amount of oily liquid obtained from the acid solution after the ketone had been isolated was not very large; it was not subjected to further investigation in this experiment. All that was established was that it yields the qualitative reaction for a hydroxyl group and that acetophenone is formed when an effort is made to distill it in vacuo. It was investigated in greater detail in Experiment III.

Investigation of Substance with m.p. of 125-127° (IV)

The substance is soluble in dilute as well as concentrated acids, with beautiful bright orange-green fluorescence. Upon neutralization the acid settles out as a white precipitate, which decolorizes an aqueous solution of potassium permanganate and a solution of bromine in chloroform very slowly; in a hydrochloric-acid solution it forms bright-yellow stable precipitates with aqueous solutions of platinum and auric chlorides.

Analysis of Substance with 125-127° m.p.

0.0952 g substance: 0.2936 g CO_2; 0.0529 g H_2O.
0.0967 g substance: 0.2971 g CO_2; 0.0539 g H_2O.
0.2672 g substance: 17.17 g C_6H_6: Δt 0.25°.
Found %: C 84.11, 83.79; H 6.18, 6.19; M 311.
Calculated %: C 84.15; H 6.09; M 328.

Determination of the number of hydroxyl groups by the Terentyev method:

0.0527 g substance: 3.5 ml CH_4 (21°, 763 mm).
Found : v_0 3.2 ml, % OH 6.07.
$C_{23}H_{19}O(OH)$. Calculated : v_0 3.6 ml, % OH 6.83.

The chloroplatinate was obtained as an orange precipitate that decomposed at 171-173°.

0.0854 g substance: 0.1614 g CO_2; 0.0308 g H_2O.
0.1501 g substance: 0.0271 g Pt.
0.0824 g substance: 0.0150 g Pt.
Found %: C 51.54; H 4.01; Pt 18.05, 28.20.
$[(C_{23}H_{20}O_2)H]_2PtCl_6$. Calculated %: C 51.27; H 3.59; Pt 18.31.

The chloroaurate was a bright-yellow substance that decomposed at 171-176°.

0.0976 g substance: 0.1477 g CO_2; 0.0279 g H_2O.
0.0914 g substance: 0.0270 g Au.
0.1010 g substance: 0.0297 g Au.
Found %: C 41.36; H 3.17; Au 29.54, 29.50.
$[(C_{22}H_{20}O_2)H]AuCl_4$. Calculated %: C 41.32; H 3.16; Au 29.49.

The properties of the substance with a m.p. of 125-127° indicate that it is a substituted hydroxydihydrofuran and is completely analogous in structure to the substituted hydroxydihydrofuran synthesized by us earlier [2,3,4].

The complete ketal of the hydroxydihydrofuran was synthesized from 0.6 g of the substance, dissolved in 6 ml of absolute alcohol with two drops of glacial acetic acid. The reaction mixture was heated to boiling for 10 minutes, after which it was set aside to stand for 24 hours at room temperature. Then half the alcohol was driven off, and the residue washed with a dilute soda solution and extracted with ether. After the ether had been driven off the residue was a rapidly thickening oil, which did not crystallize in the course of two weeks, however.

0.1725 g substance: 0.5316 g CO_2; 0.1082 g H_2O.
0.1461 g substance: 0.0966 g AgI
Found %: C 84.16; H 6.96; OC_2H_5 12.70.
$C_{23}H_{19}O(C_2H_5)$. Calculated %: C 84.27; H 6.72; OC_2H_5 12.64.

Mineral acids quickly decomposed the ketal, converting it into colored oxonium salts of the initial substituted hydroxydihydrofuran.

Experiment II. Action of 30% Sulfuric Acid on the Pinacol

13 g of the pinacol was heated with 130 ml of 30% sulfuric acid. The subsequent procedure was the same as in experiment I.

We obtained 3.3 g of a ketone with a m.p. of 95-96° (37% of theory), 2 g of the substituted hydroxydihydrofuran with a m.p. of 125-127° (15.4% of theory) and – after separation of the ketone – 6.7 g of an oily liquid.

Experiment III. Action of 20% Sulfuric Acid on the Pinacol

23 g of pinacol was used with 10 times the quantity of 20% sulfuric acid. The test conditions were like those in the preceding experiments. As the mixture was stirred and warmed up, the aqueous layer turned greenish in color, but no markedly evident fluorescence was observed.

The ether extract of the acid solution yielded an oil, from which 2.2 g of the ketone with a m.p. of 96-97° (10.3% of theory) was isolated after the oil had been stirred with alcohol.

After the ketone had been eliminated and the alcohol driven off, we obtained 18.5 g of a dark-yellow oily liquid. Neutralization of the acid solution, after elimination of the ketone and the oily liquid, caused the color of the solution to vanish, and traces of a solid substance settled out, contaminated by a reddish impurity. We consider this substance to be the substituted hydroxydihydrofuran described in Experiment I.

Investigation of the Liquid Isolated from the Acid Solution (III)

The substance exhibits the qualitative reaction for hydroxyl groups, easily decolorizing an aqueous solution of potassium permanganate and bromine water, and not forming a semicarbazone under ordinary conditions.

It is cleaved, like the pinacol, upon vacuum distillation. Thus, when 8.5 g of the substance was distilled, we obtained the following fractions:

1st fraction, b.p. 73-83°, pressure 7.5 mm – 1.7 g,
2nd fraction, b.p. 180-210°, pressure 4 mm – 2.5 g.

The first fraction exhibited the strong odor of acetophenone, yielded a semicarbazone with a m.p. of 200-201° without residue, and caused no depression of the melting point when mixed with a known sample of the semicarbazone of acetophenone.

The second fraction was a yellow liquid, which solidified into thin long needles with a m.p. of 55-56° when rubbed with petroleum ether. Two grams of this substance were mixed with 2 g of phenylhydrazine and heated for 1 hour over a water bath. Upon cooling a yellow substance precipitated out, which melted at 134-135° after fourfold recrystallization from alcohol and acetic acid. This substance exhibits the pyrazoline reaction (conc. H_2SO_4 and $NaNO_2$) and caused no depression of the melting point when mixed with the 1,3,5-triphenylpyrazoline (XIV) synthesized by us from benzalacetophenone (XIII).

The m.p. cited in the literature for benzalacetophenone is 57-58°, and for 1,3,5-triphenylpyrazoline [10] is 134-135°.

The cleavage of the liquid product of the isomerization of the pinacol into acetophenone and benzalacetone indirectly confirms its structure as an unsaturated γ-ketone alcohol (III).

The substance was oxidized to confirm its structure.

Oxidation was effected with an aqueous solution of potassium permanganate, first at room temperature, but toward the end heated to 50°, until the solution turned completely colorless. A solution of 2.5 g of potassium permanganate in 200 ml of water was added to 3.6 g of the substance, with vigorous stirring. Five hours later the remaining 2.4 g of the oxidant was added in small batches as a crushed powder. After 24 hours of stirring in the cold the reaction mass was heated to 50° for six hours.

The neutral products of oxidation that distilled off with steam contained 0.5 g of acetophenone, identified by its semicarbazone with a m.p. of 200-201°. The neutral substance that was not driven off with the steam, with a m.p. of 65-66°, caused no depression of the melting point when mixed with a known sample of methyl benzoate.

When acidulated with salts of organic acids, benzoic acid separates out; the acid was identified by the melting point of a mixed sample with known benzoic acid. After the benzoic acid had been drawn off, the organic acids that remained in solution were extracted with ether; after the latter had been driven off they had an unsharp m.p. (60-106°). When phenylhydrazine hydrochloride was added to an aqueous solution of this substance, a flocculent precipitate settled out, which melted at 151-152.5° after recrystallization from acetic acid. A melting point of 153° is given in the literature [14] for the condensation product of benzoylformic acid and phenylhydrazine.

The small quantity of this substance obtained was not subjected to closer investigation.

The oxidation products: methyl benzoate, acetophenone, benzoic and benzoylformic acid, confirm the assumed structure of an unsaturated γ-ketone alcohol.

III. Action of 40% Sulfuric Acid on the Unsaturated γ-Ketone Alcohol

Using dimethylphenyl-tertiary-butylacetylenylethylene glycol as an example, it was established [4] that increasing the concentration of acid enables us to effect the partial cyclization of an unsaturated γ-ketone alcohol into a substituted hydroxydihydrofuran, yielding with the acid a water-soluble, highly fluorescent sulfate.

In the present instance, heating 3 g of the γ-ketone alcohol with 30 ml of 40% sulfuric acid caused the solution to turn yellow, with strong orange-green fluorescence. When the acid solution was neutralized, 1 g of a substance was isolated, which melted at 125-127° after recrystallization, and whose properties indicated it was a substituted hydroxydihydrofuran. The yield was 33.3% of theory, based on the γ-ketone alcohol consumed.

SUMMARY

1. Methyldiphenyl-phenylacetylenylethylene glycol (2,3,5-triphenylpentyne-4-diol-2,3) was synthesized.

2. The ketonic cleavage of 2,3,5-triphenylpentyne-4-diol-2,3 into acetophenone and 1,3-diphenylpropyn-1-ol-3 upon heating in vacuum was discovered.

3. The action of 20, 30, and 40% sulfuric acid upon 2,3,5-triphenylpentyne-4-diol-2,3 was investigated. Among the transformation products we found: an acetylenic ketone – 3,3,5-triphenylpentyn-4-one-2; an unsaturated γ-ketone alcohol – 2,3,5-triphenylpenten-3-ol-2-one-5; and 2,4,5-triphenyl-5-methyl-2-hydroxydihydrofuran-2,5.

4. The transformation products indicate that two types of transformation occur simultaneously: a pinacolin and an acetylene-allene rearrangement.

5. It was established that as the acid concentration is raised the yield of the ketone and of the substituted hydroxydihydrofuran likewise rises.

6. The conversion of the γ-ketone alcohol into the substituted hydroxydihydrofuran by the action of 40% sulfuric acid was established.

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THE DERIVATIVES OF ACETYLENE

101. SYNTHESIS OF POLYCYCLIC COMPOUNDS WITH AN ANGULAR METHYL GROUP. II

Condensation of 2,2-Dimethyl-4-Vinyl-3,6-Dihydropyran with 1,3-Dimethyl-1-Cyclopenten-5-one- and 1,3-Dimethyl-1-Cyclopentene-4,5-dione.

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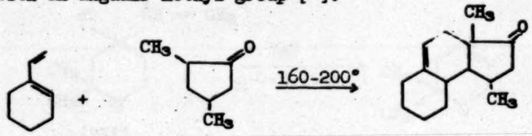
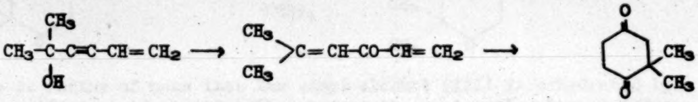
Institute of Organic Chemistry of the USSR Academy of Sciences

The present paper is part of a broad plan of research undertaken by our laboratory for the synthesis of the polycyclic ketones related to the steroids. We recently effected the condensation of vinylcyclohexene with 1,3-dimethyl-1-cyclopenten-5-one, resulting in the corresponding tricyclic ketone with an angualr methyl group [1].



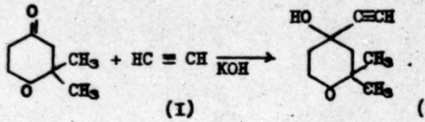
The synthesis of heterocyclic ketones by this same method, especially the ketones that contain the pyran ring, seemed to be of some interest.

The compound that served as the initial product was the available 2,2-dimethyltetrahydro-4 pyrone (I), which is easily synthesized by isomerizing dimethylvinylethylcarbinol and hydrating the resulting β,β-dimethyldivinyl ketone [2]:

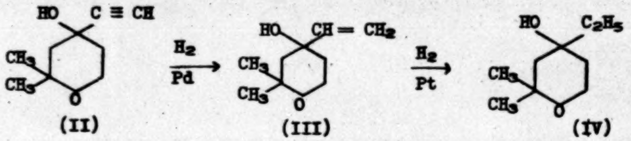


(I)

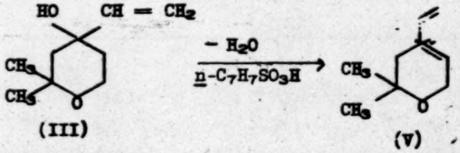
When the pyrone (I) was condensed with acetylene in the presence of powdered caustic potash, we obtained 2,2-dimethyl-4-ethyltetrahydro-4-pyranole (II) with a yield of 30%:


O
CH3
CH3
O
+ HC ≡ CH
KOH
HO
C≡CH
CH3
CH3
O
(I)
(II)

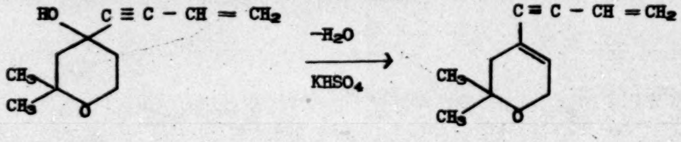
Partial hydrogenation of the ethylpyranole (II) in the presence of a palladium catalyst yielded 2,2-dimethyl-4-vinyltetrahydro-4-pyranol (III), while complete hydrogenation with a Pt catalyst by the Adams method yielded 2,2-dimethyl-4-ethyltetrahydro-4-pyranole (IV):


HO
C ≡ CH
CH3
CH3
O
(II)
H2
Pd
HO
CH = CH2
CH3
CH3
O
(III)
H2
Pt
HO
C2H5
CH3
CH3
O
(IV)

2,2-dimethyl-4-vinyl-3,6-dihydropyran (V) was synthesized with a yield of 68% by the dehydration of the vinylpyranole (III) by means of p-toluenesulfonic acid:

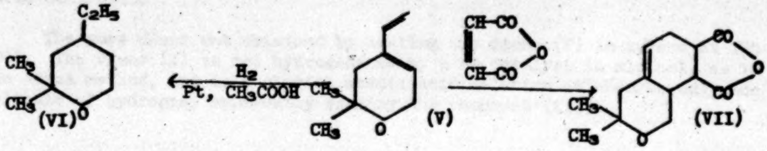

HO
CH = CH2
CH3
CH3
O
(III)
− H2O
n-C7H7SO3H
CH3
CH3
O
(V)

The position of the double bond in the dienc (V) was established by analogy with the dehydration of 2,2-dimethyl-4-vinylethynyltetrahydro-4-pyranole, where we proved that the double bond exists in the ring only at the 4,5 position [3]:


HO
C ≡ C − CH = CH2
CH3
CH3
O
−H2O
KHSO4
C ≡ C − CH = CH2
CH3
CH3
O

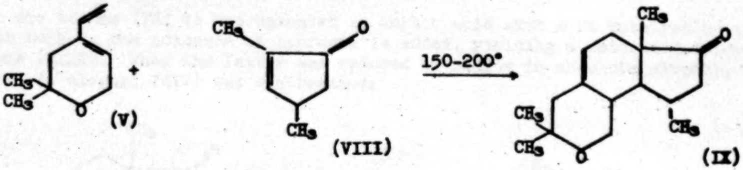
It is worthy of note that the vinyl alcohol (III) is dehydrated by p-toluenesulfonic acid at 110-115°, whereas the acetylenic alcohol (II) remains unchanged under these conditions, being dehydrated only at a temperature of 180-190°.

When the diene (V) is hydrogenated in glacial acetic acid we get 2,2-dimethyl-4-ethyltetrahydro-4-pyran (VI), and when it is condensed with maleic anhydride the corresponding addition compound (VII) is obtained:

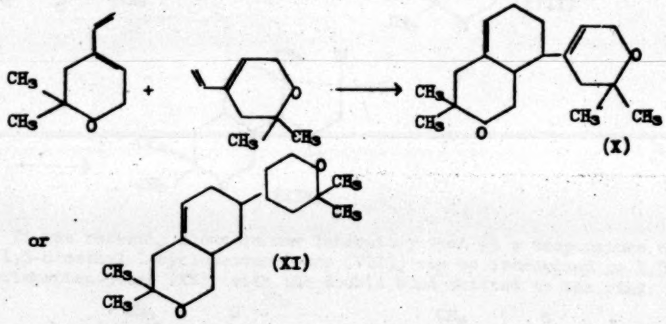

C2H5
CH3
CH3
(VI)
H2
Pt, CH3COOH
CH3
CH3
(V)
CH-CO
CH-CO
CH3
CH3
(VII)

It should be noted that the diene (V) is not 100% hydrogenated with a Pt catalyst in an alcohol solution.

At temperatures above 150° the diene (V) easily enters into condensation reaction with 1,3-dimethyl-1-cyclopenten-5-one (VIII), forming a tricyclic ketone (IX):


CH3
CH3
(V)
CH3
CH3
(VIII)
150-200°
CH3
CH3
CH3
CH3
(IX)

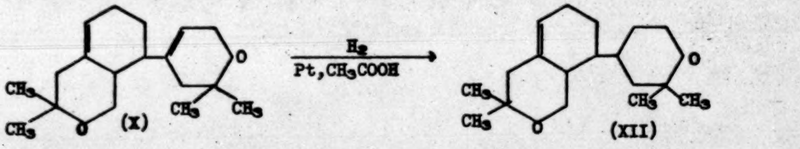
At the same time the diene (V) is dimerized:


CH3
CH3
CH3
CH3
CH3
CH3
CH3
CH3
(X)
or
CH3
CH3
CH3
CH3
(XI)

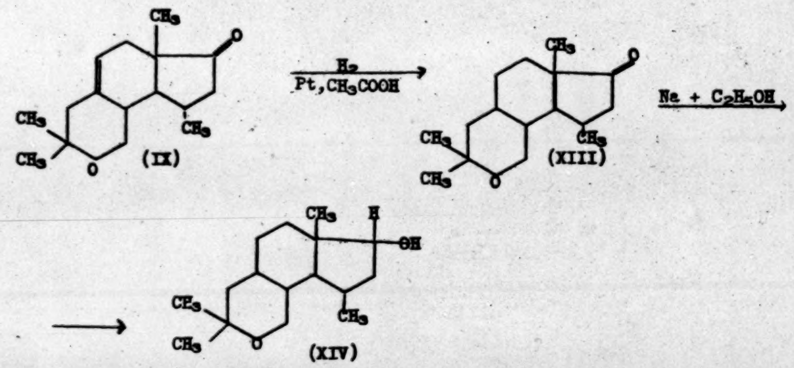
By analogy with the dimerization of vinylcyclohexene [1], the most probable structure of the dimer is that represented by formula (X).

Condensation of the diene (V) with the ketone (VIII) yields a tricyclic ketone (IX) with traces of the dimer (X). It is extremely difficult to separate them owing to the closeness of their boiling points. The percentage of the dimer rises somewhat when the reaction temperature is raised, and hence the purest tricyclic ketone is obtained when the condensation of the diene (V) and the ketone (VIII) is effected with an excess of the latter at temperatures of 160-185°.

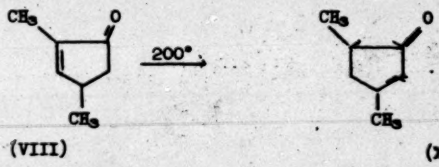
The pure dimer was obtained by heating the diene (V) in xylene at 195-200°. The dimer (X) is not hydrogenated by a Pt catalyst in alcohol, as in the Adams method, and in a glacial acetic acid solution it absorbs only one molecule of hydrogen, apparently forming the compound (XII):


CH3
CH3
O
(X)
CH3
CH3
O
H2
Pt,CH3COOH
CH3
CH3
O
O
CH3
CH3
(XII)

When the ketone (IX) is hydrogenated in acetic acid with a Pt catalyst by the Adams method, one molecule of hydrogen is added, yielding a saturated tricyclic ketone (XIII). When the latter was reduced by sodium in absolute alcohol, the tricyclic alcohol (XIV) was synthesized:

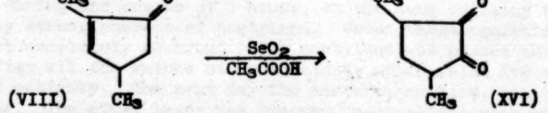

CH3
O
CH3
CH3
CH3
O
(IX)
H2
Pt,CH3COOH
CH3
O
CH3
CH3
CH3
O
(XIII)
Na + C2H5OH
CH3
H
OH
CH3
CH3
CH3
O
(XIV)

It was recently shown in our laboratory that at a temperature of about 200° 1,3-dimethyl-1-cyclopenten-5-one (VIII) can be isomerized to 1,3-dimethyl-3-cyclopenten-5-one (XV), with the double bond shifted in the ring:

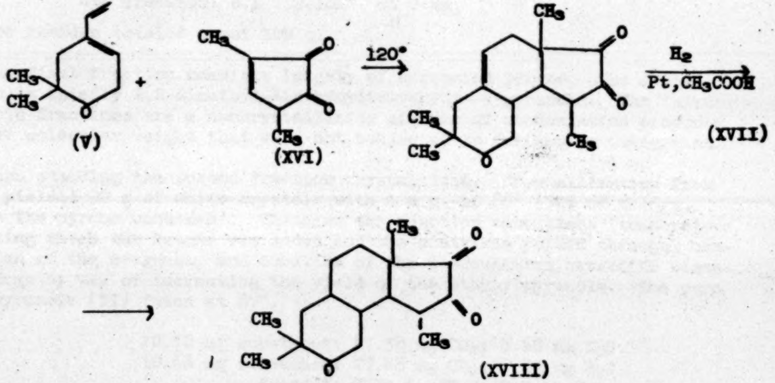

CH3
O
CH3
(VIII)
200°
CH3
O
CH3
(XV)

It therefore appeared desireable to learn whether the ketone (XV) can also be condensed with the diene (V). To clear up this matter, the diene (V) was heated with the ketone (XV) under the same conditionn as were used for the ketone (VIII). The condensation product, however, contained only the one dimer (X), which doubtless indicates that the ketone (XV) is considerably less reactive in the diene synthesis than the ketone (VIII). Therefore, although the ketone (VIII) is partially isomerized when heated with the diene (V), it is the ketone (VIII) that enters into the condensation reaction and not the ketone (XV) that is formed from it.

The condensation of the diene (V) with 1,3-dimethyl-1-cyclopentene-4,5-dione (XVI), which we synthesized with a yield of 35% by oxidizing the ketone (VIII) with selenium oxide in glacial acetic acid [5], takes place under much milder conditions:



The presence of two carbonyl groups in compound (XVI) is responsible for the increased reactivity of the double bond in the diene synthesis, and that is why the condensation of the diene (V) with the cyclopentenedione (XVI) takes place easily even at 120°, yielding as its sole product a tricyclic diketone (XVII):



Hydrogenation of the latter in acetic acid yields the saturated tricyclic diketone (XVIII). Both diketones, (XVII) and (XVIII), are colorless, crystalline substances They are insoluble in water and basic carbonates, but, like the phenols, they dissolve easily in caustic alkalies, from which they precipitate unchanged upon acidulation. Neither forms crystalline quinoxalines with phenylenediamine, which indicates the complete enolization of compounds (XVII) and (XVIII).

EXPERIMENTAL

2,2-Dimethyltetrahydro-4-pyrone was obtained by the isomerization and hydration of dimethylvinylethynylcarbinol as described previously [3]; its constants were as follows:

B.p. 177-180°; n_D^{20} 1.4470.

Condensation of 2,2-Dimethyltetrahydro-4-pyrone with Acetylene

A suspension of 180 g of powdered caustic soda in 1600 ml of absolute ether, well-stirred and chilled to -10°, was saturated with acetylene, the time required being about one hour. Then 266 g of 2,2 dimethyltetrahydro-4--pyrone were added during the course of 6 hours, at the same chilling temperature and in a fairly strong current of acetylene. Under these conditions the acetylene was almost completely absorbed. The acetylene was passed through for 3 more hours after all the ketone had been added, after which its absorption stopped almost entirely. The next day the mixture, chilled, was treated with 300 ml of water. The ether layer was removed, neutralized with sulfuric acid (1:2), and washed three times with small amounts of water. After the ether had been driven off, the water and a small amount of the pyrone were driven off in a vacuum of 25 mm, and the residue was fractionated at 2 mm.

1st fraction: b.p. 40-78°	at 2 mm,	23 g,
2nd fraction: b.p. 79-84°	at 2 mm,	122 g,
3rd fraction: b.p. 85-152°	at 2 mm,	7 g,
4th fraction: b.p. 152-162°	at 2 mm,	6 g.

The residue totaled about 100 g.

The first fraction consists largely of unreacted pyrone. The second fraction is chiefly 2,2-dimethyl-4-ethynyltetrahydro-4-pyranole. The third and fourth fractions are a noncrystallizing mixture of condensation products of higher molecular weight that were not subjected to further investigation.

Upon standing the second fraction crystallized. Crystallization from benzene yielded 92 g of white crystals with a m.p. of 86° (32% of theory, based on the pyrone consumed). Changing the reaction conditions (temperature, time during which the ketone was added and the acetylene passed through, concentration of the reagents, and duration of the condensation caused no essential change by way of increasing the yield of the ethynylpyranole. The pure ethynylpyranole (II) fuses at 87°.

10.70 mg substance: 27.58 mg CO_2; 8.68 mg H_2O.
10.68 mg substance: 27.48 mg CO_2; 8.87 mg H_2O.
Found %: C 70.3, 70.2; H 9.1, 9.3.
$C_9H_{14}O_2$. Calculated %: C 70.1; H 9.2.

The pyranole (II) has a slight odor; it dissolves fairly well in water, very well in alcohol and ether, and poorly in benzene. It underwent no change upon standing for 6 months.

Hydrogenation of the Ethylenepyranole (II)

32.5 g of the pyranole (II), dissolved in 50 ml of alcohol, was hydrogenated with a Pd catalyst until one molecule of hydrogen had been absorbed

(5.28 liters at 17° and 760 mm). Yield: 28.5 g of 2,2-dimethyl-4-vinyltetrahydro-4-pyranole (III), a thick liquid with a faint odor, that is fairly soluble in water:

B.p. 84-85° at 8 mm
106-107° at 21 mm; n_D^{20} 1.4725; d_4^{20} 0.9955; MR found 44.00; calc. 44.25.
4.900 mg substance: 12.297 mg CO_2; 4.625 mg H_2O.
Found %: C 68.5; H 10.6;
$C_9H_{16}O_2$. Calculated %: C 69.2; H 10.3.

In addition to hydrogenation, the purity of the substance was tested by heating with caustic potash to 120-130°. Only a small quantity of acetylene was generated; after distillation the substance was found to have the following constants:

B.p. 84-85° at 8 mm; n_D^{20} 1.4723; d_4^{20} 0.9949; Constants were practically unchanged.

Hydrogenation of the Vinylpyranole (III)

3.0 g of the pyranole (III) dissolved in 5 ml of alcohol was hydrogenated with a Pt catalyst. 0.46 liter of hydrogen was absorbed (22°, 761 mm), as against 0.46 liter according to theory. The end product was 2.1 g of 2,2-dimethyl-4-ethyltetrahydro-4-pyranole (IV). This was a colorless viscous liquid, almost odorless and somewhat soluble in water:

B.p. 87-87.5° at 8 mm; n_D^{20} 1.4650; d_4^{20} 0.9810; MR found 44.6; calculated 44.7.
6.445 mg substance: 16.017 mg CO_2; 6.580 mg H_2O.
6.785 mg substance: 16.903 mg CO_2; 6.813 mg H_2O.
Found %: C 67.8, 68.0; H 11.4, 11.2.
$C_9H_{18}O_2$. Calculated %: C 68.3, H 11.5.

Dehydration of the Vinylpryanole (III)

In a 100 ml Claisen flask there were placed 37 g of the pyranole (III), 1 g of p-toluenesulfonic acid, and 0.1 g of pyrogallol. The mixture was heated in a vacuum of 28-30 mm. Dehydration commenced at 100-105°, and the heating was adjusted so that the temperature of the exit vapors was 67-75°. Toward the end the bath temperature was raised to 130°. Two runs yielded a total of 58 g of distillate (of which 8 g represented water). After drying and fractional distillation we got 40 g of the diene (V), with a b.p of 83-85° at 40 mm. Redistillation with steam of the residues left after dehydration yielded another 5 g of a less pure product. The overall yield of the diene (V) was 68%. The diene (V) is a colorless liquid with a pleasant odor that is insoluble in water.

B.p. 83-85° at 40 mm; 65-67° at 19 mm; 46-48° at 8 mm; n_D^{20} 1.4840; d_4^{20} 0.9051;
MR found 43.7; calculated 42.3.
5.671 mg substance; 16.249 mg CO_2; 5.199 mg H_2O.
5.464 mg substance; 15.609 mg CO_2; 4.994 mg H_2O
Found %: C 78.2, 78.0; H 10.3, 10.2.
$C_9H_{14}O$. Calculated %: C 78.2; H 10.2.

The diene (V) remained unchanged during three months of storage in the presence of 0.5% of pyrogallol.

Hydrogenation of the Diene (V)

3.4 g of the diene, dissolved in 10 ml of glacial acetic acid (hydrogenation is not 100% in alcohol), was hydrogenated in the presence of a Pt catalyst by the Adams method. 1.11 liters of hydrogen were absorbed (20°, 760 mm) as against 1.18 liters according to theory. Neutralization with a 10% solution of caustic potash, extraction with ether, and distillation yielded 2.6 g of 2,2-dimethyl-4-ethyltetrahydropyran (VI). This is a colorless liquid with a pleasant odor that is insoluble in water:

B.p. 70° at 31 mm;
n_D^{20} 1.4338; d_4^{20} 0.8550; MR found 43.3; calculated 43.2.

4.780 mg substance: 13.340 mg CO_2; 5.342 mg H_2O.
Found %: C 76.1; H 12.5.
$C_9H_{18}O$. Calculated %; C 76.0; H 12.8.

Condensation of the Diene (V) with Maleic Anhydride

A solution of 2.8 g of the diene (V) and 2.0 g of maleic anhydride in 5 ml of anhydrous benzene was heated for 8 hours in a sealed tube at 125-130°. The contents of the tube crystallized upon standing after cooling. Yield: 2.0 g of a product (VII) as colorless crystals with a m.p. of 148-149° (from benzene):

4.272 mg substance: 10.343 mg CO_2; 2.612 mg H_2O.
3.920 mg substance: 9.503 mg CO_2; 2.448 mg H_2O.
Found %: C 66.0; 66.1; H 6.8, 7.0.
$C_{13}H_{14}O_4$. Calculated %: C 66.1; H 6.8.

To determine the molecular weight, 0.1266 g of the substance was heated with 17.11 ml of 0.1 N KOH until complete dissolution. In back titration, 6.61 ml of 0.1 N H_2SO_4 were used.
Found: M 234; computed: 236.

Dimerization of the Diene (V)

A solution of 4.9 g of the diene in 5 ml of xylene was heated with a small quantity of pyrogallol in a sealed tube for [illegible] hours at [illegible]. After distillation 1.7 g of the dimer (X or XI) was obtained as a very thick, colorless, odorless liquid that was insoluble in water [illegible]
[illegible]

B.p. 131-132° at 2 mm; n_D^{20} 1.5078; d_4^{20} 1.0155; MR found 81.1; calculated 81.1.

6.465 mg substance: 18.506 mg CO_2; 5.930 mg H_2O.
4.075 mg substance: 11.680 mg CO_2; 3.760 mg H_2O.
Found %: C 78.1, 78.2; H 10.3, 10.3.
$C_{18}H_{28}O_2$. Calculated %: C 78.2; H 10.2.

Hydrogenation of the Dimer (X)

1.45 g of the dimer, dissolved in 6 ml of glacial acetic acid was hydrogenated with a Pt catalyst by the Adams method. 125 ml of hydrogen (23°, 760 mm) were absorbed as against the 130 ml required by theory. The yield was 0.9 g of compound (XII). This was a colorless, viscous liquid, with a very faint pleasant odor, insoluble in water:

B.p. 142-144° at 2.5 mm; n_D^{20} 1.4990; d_4^{20} 1.0050; MR found 81.4; calculated 81.5.

3.870 mg substance: 11.019 mg CO_2; 3.770 mg H_2O.
4.225 mg substance: 12.009 mg CO_2; 4.099 mg H_2O.
Found %: C 77.7, 77.6; H 10.9, 10.9.
$C_{18}H_{30}O_2$. Calculated %: C 77.7; H 10.9.

Condensation of 1,3-Dimethyl-1-cyclopenten-5-one with the Diene (V)

8 g of the diene (V), 31 g of the ketone (VIII) (b.p. 60-62° at 16 mm; n_D^{20} 1.4687), and 0.025 g of pyrogallol were heated in an atmosphere of carbon dioxide in a sealed tube for 10 hours at 180-184°. Four such tests were run in all. Fractional distillation yielded the following results:

1st fraction: 64-70° at 19 mm, 124 g; n_D^{20} 1.470;
2nd fraction: 45-130° at 3 mm, 4 g;
3rd fraction: 130-136° at 3 mm, 20 g; n_D^{20} 1.5096; d_4^{20} 1.0395.

Fraction 1 consists of the initial ketone (VIII), the unreacted diene (V), and, possibly, a small amount of the ketone (XV).

Fraction 3 is the tricyclic ketone (IX) with some 15-20% of the dimer. Repeated redistillation of this fraction yielded 6.3 g of the tricyclic ketone (IX) with the highest specific gravity. This is a thick colorless, odorless liquid that is insoluble in water:

B.p. 123-125° at 2 mm; n_D^{20} 1.5091; d_4^{20} 1.0434; MR found 71.1; calculated 70.7.

7.340 mg substance: 20.848 mg CO_2; 6.410 mg H_2O.
6.960 mg substance: 19.743 mg CO_2; 6.150 mg H_2O.
Found %: C 77.5, 77.4; H 9.8, 9.9.
$C_{16}H_{24}O_2$. Calculated %: C 77.4; H 9.7.

The synthesized tricyclic ketone (IX) remained unchanged for 3 months.

Diene-synthesis tests, run at 200° (10 hours), yielded the tricyclic ketone (IX) with a high percentage of the dimer (about 30%) and, hence, with a lower specific gravity (1.037). Tests run at 150-160° yielded a product with a sp.gr. of 1.041, but with a lower yield (20% for 60 hours of heating).

The semicarbazone of the tricyclic ketone (IX) was synthesized by boiling the ketone for 15 hours with a threefold excess of semicarbazide acetate in an alcohol solution.

The crystals that settled out were a mixture of disemicarbazide (m.p. 242-273°) and the sought-for semicarbazone. The latter is easily isolated because of its high solubility in alcohol. The colorless crystals have a m.p. of 219-220° (from alcohol).

4.710 mg substance: 0.586 ml N_2 (21°, 755 mm)
5.370 mg substance: 0.670 ml N_2 (21°, 759 mm).
Found %: N 14.3, 14.5.
$C_{17}H_{27}O_2N_3$. Calculated %: N 13.8.

We were unable to synthesize the crystalline dinitrophenylhydrazone. We got the oxime as an oil that distills at 150-155° at 2 mm as an extremely viscous colorless liquid, which was not investigated further.

Hydrogenation of the Tricyclic Ketone (IX)

3.8 g of the ketone, dissolved in 10 ml of glacial acetic acid, was hydrogenated with a Pt catalyst by the Adams method. Hydrogenation was slow, being completed in 6 hours. It absorbed 0.4 liter of hydrogen (20°, 760 mm), as against the 0.37 liter required by theory. The end product was a saturated tricyclic ketone (XIII) in the form of a viscous, colorless liquid with a very faint odor, which was insoluble in water:

B.p. 131-133° at 2.5 mm; n_D^{20} 1.5007; d_4^{20} 1.0370; MR found 71.1; calculated 71.1.

5.680 mg substance: 16.073 mg CO_2; 5.408 mg H_2O.
4.700 mg substance: 13.278 mg CO_2; 4.420 mg H_2O.
Found %: C 77.1, 77.1; H 10.6, 10.5.
$C_{16}H_{26}O_2$. Calculated %: C 76.8; H 10.5.

The semicarbazone was synthesized under the same conditions as those used for the ketone (IX). The colorless crystals fused with decomposition at 232-235° (from alcohol):

4.240 mg substance: 0.528 ml N_2 (20°, 760 mm).
Found %: N 14.1.
$C_{17}H_{29}O_2N_3$. Calculated %: N 13.7.

We were unable to synthesize the crystalline dinitrophenylhydrazone.

Reduction of the Ketone (XIII) to the Alcohol (XIV)

1.9 g of the ketone (XIII) in 50 ml of boiling absolute alcohol was reduced with 5 g of sodium. Neutralization with acetic acid, driving off of the alcohol *in vacuo*, extraction, and distillation yielded 1.5 g of the alcohol (XIV) as a thick colorless liquid with a faint odor, which was insoluble in water:

B.p. 124-127° at 2 mm; n_D^{20} 1.5039; d_4^{20} 1.0323; MR found 72.3; Calculated 72.6.

10.32 mg substance: 28.78 mg CO_2; 10.18 mg H_2O.
10.25 mg substance: 28.59 mg CO_2; 10.25 mg H_2O.
Found %: C 76.1, 76.1; H 11.0, 11.2.
$C_{16}H_{28}O_2$. Calculated %: C 76.1; H 11.2.

The dinitrobenzoate of the alcohol (XIV) is in the form of pale green crystals (from benzene) with a m.p. of 177-177.5° (corrected):

6.393 mg substance: 2.82 ml 0.01 N H_2SO_4.
4.502 mg substance: 2.04 ml 0.01 N H_2SO_4.
Found %: N 6.2, 6.3.
$C_{23}H_{30}O_7N_2$. Calculated %: N 6.7.

Determination of hydroxyl groups in the alcohol (XIV) by the Zerewitinoff method:

0.2096 g substance: 16.9 ml CH_4 (16°, 725 mm).
0.1872 g substance: 15.1 ml CH_4 (16°, 725 mm).
Found %: OH 5.53, 5.56.
$C_{16}H_{27}O(OH)$. Calculated %: OH 6.75.

The data obtained indicate that the alcohol (XIV), as well as the initial ketone (XIII), contains about 15% of the dimer (X). A similar determination of hydroxyl groups in the alcohol (XIV) synthesized from the ketone (XIII) with a sp. gr. of 1.037 yielded a dimer percentage of 35%. So high a percentage of the dimer (X) in the alcohol (XIV) in this case is the reason why this sample does not yield a crystalline dinitrobenzoate.

Condensation of the Diene (V) with 1,3-Dimethyl-3-cyclopenten-5-one (XV)

The cyclopentenone (XV) was synthesized by isomerizing the cyclopentenone (VIII) by the method described previously [4].

A mixture of 7.6 g of the diene (V) and 16.4 g of the ketone (VII) (b.p. 180-182°; n^{20} 1.4772) was heated for 10 hours with 0.25 g of pyrogallol in a carbon-dioxide atmosphere within a sealed tube at 180-185°. Fractional distillation yielded the following results:

1st fraction: b.p. 53-60° at 8.5 mm, 17.9 g; n_D^{20} 1.4766;
2nd fraction: b.p. 61° at 8.5 mm, 132° at 2 mm, 0.5 g;
3rd fraction: b.p. 132-134° at 2 mm, 2.6 g; n_D^{20} 1.5099.
Residue ... 2.5 g.

Fraction 1 is the initial cyclopentenone (XV). Fraction 3 is a thick colorless, odorless liquid. To judge by its specific gravity (d_4^{20} 1.0195), it consists of at least 90% of the dimer (X). Hence, the ketone (XV) reacts with the diene (V) much more slowly than does the ketone (VIII), which yields the tricyclic ketone (IX) under these conditions, with an admixture of only 15% of the dimer.

Synthesis of 1,3-Dimethyl-1-cyclopentene-4,5-dione (XVI)

A suspension of 37 g of selenium dioxide in a mixture of 46 g of glacial acetic acid and 36 g of 1,3-dimethyl-1-cyclopenten-5-one (VIII) was heated with constant stirring and an air-cooled reflux condenser. A violent reaction set in at 100-110°, and the flask had to be cooled with water to make the boiling more quiet. Then the mixture was boiled for a further half-hour, cooled, filtered, andvacuum-distilled. At 85-105° (3mm) the diketone (XVI) distilled over, solidifying into yellow crystals in the receiver. The distillate weighed 17.5 g. Recrystallization from a mixture of benzene and cyclohexane yielded 13.7 g of the diketone (XVI) with a m.p. of 63-64°, which was quite adequate for further operations. The pure diketone (XVI) melted at 67°. Its quinoxaline fused at 253-254° with decomposition.

Condensation of the Diene (V) with the Diketone (XVI)

7.6 g of the diene (V) and 6.5 g of the diketone (XVI), dissolved in 5 ml of anhydrous dioxane were heated in a sealed tube in a carbon-dioxide atmosphere at 120-125° for 10 hours. After the dioxane had been driven off *in vacuo*, the residue crystallized. Crystallization from benzene yielded 4.1 g of the tricyclic diketone (XVII), colorless crystals with a m.p. of 169-170°.

12.49 mg substance: 33.79 mg CO_2; 9.68 mg H_2O.
10.01 mg substance: 27.03 mg CO_2; 7.61 mg H_2O.
Found %: C 73.8, 73.7; H 8.7, 8.5.
$C_{16}H_{22}O_3$. Calculated %: C 73.2; H 8.5.

The diketone (XVII) is insoluble in water and soda solution, but dissolves easily in 3-5% caustic potash, from which it is precipitated unchanged by acidulation. It dissolves well in acetic acid as well as in hot alcohol and benzene. It does not form a quinoxaline with o-phenylenediamine.

Hydrogenation of the Tricyclic Diketone (XVII)

4.1 g of the diketone in 15 ml of glacial acetic acid was hydrogenated by the Adams method with a Pt Catalyst. Hydrogenation was [illegible] rapid, being completed in 20 minutes. It absorbed 0.36 liter of hydrogen (17°, 760 mm), as against the 0.37 liter required by theory. After filtration, the acetic acid was driven off *in vacuo*, at 20°; then 20 ml of water was added, and the latter, together with the residue of acetic acid, driven off *in vacuo* to dryness. This precaution prevents the product from turning pink, which always occurs during further treatment in air if all the acetic acid has not been carefully eliminated. Crystallization of the residue from alcohol yielded 3.65 g of a saturated tricyclic diketone (XVIII). Colorless crystals with a m.p. of 129.5-130°.

10.15 mg substance: 27.23 mg CO_2; 8.47 mg H_2O.
10.88 mg substance: 29.10 mg CO_2; 8.88 mg H_2O.
Found %: C 73.2, 73.0; H 9.3, 9.1.
$C_{16}H_{24}O_3$. Calculated %: C 72.7; H 9.1.

The diketone (XVIII) is insoluble in water, and in solutions of alkali hydroxides and basic carbonates it behaves like the diketone (XVII). It dissolves well in acetic acid and in hot alcohol and benzene. It forms no quinoxaline with o-phenylenediamine.

SUMMARY

1. Condensation of 2,2-dimethyltetrahydro-4-pyrone (I) with acetylene in the presence of powdered caustic potash yields 2,2-dimethyl-4-ethyltetrahydro-4-pyranole (II) with a yield of 30%, which, when partially hydrogenated with a Pd catalyst, is converted into the corresponding vinyltetrahydropyranole (III); dehydration of the latter with the aid of p-toluenesulfonic acid results in a yield of 68% of vinyldihydropyran (V) with conjugated double bonds.

2. Vinyldihydropyran (V) condenses easily with maleic anhydride, forming an addition product (VII). At a temperature of 160-185° the vinyldihydropyran (V) also condenses easily with 1,3-dimethyl-1-cyclopenten-5-one (VIII), forming a tricyclic ketone of the pyranole series (IX), which contains a cyclopentanone ring with an angular methyl group.

3. Oxidation of the 1,3-dimethyl-1-cyclopenten-5-one (VII) by selenium oxide in a solution of glacial acetic acid yields the corresponding cyclopentenedione(XVI), which condenses with the vinyldihydropyran (V) at temperatures as low as 120°, forming a tricyclic diketone (XVII).

4. At temperatures in the neighborhood of 200°, the vinyldihydropyran (V) is dimerized fairly easily, forming a dimer (X or XI).

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THE DERIVATIVES OF ACETYLENE

102. MECHANISM OF HYDRATION AND CYCLIZATION OF THE DIENES

XX. Hydration and Cyclization of Di-Δ^1-Cyclohexenyl-Acetylene and 1,2-Dicyclohexyl-1,5-Hexadien-3-Yne

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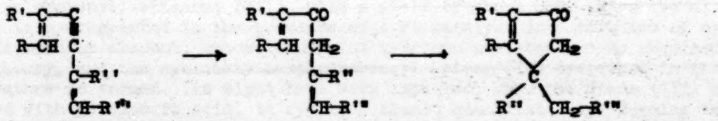
For the past eight years our laboratory has been engaged in the systematic investigation of the hydration and cyclization reactions of various mono-, di-, tri-, and tetra- substituted dienes [1].

It was shown that these reactions always result in the formation of nothing but the corresponding substituted cyclopentenones; no cyclohexenones were observed, contrary to the assertion of Marvel and his associates [2]

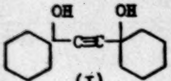


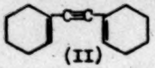
The problem of the structure of the cyclic ketones synthesized by Marvel through the cyclohydration of di- Δ^1-cyclohexenylacetylene (II) aroused special interest and prolonged discussion. Basing himself on an incorrect mechanism of the cyclohydration of the dienes, Marvel ascribed the structure of 9-dodecahydrophenanthrone [3] to this ketone, at first assuming it had the formula (V), but later assigning the formula (VI), after the researches of Linstead and Walpole [4].

Subsequently, however, Bogert pointed out [5] that Marvel's so-called ketone actually contains 1,1-spirocyclohexane-Δ^1-tetrahydroindan-3-one (VII).

The definitive proof that Marvel's ketone is not a derivative of phenanthrene but a spiran (VII) was supplied by the researches of Linstead and his associates [6].

Thus, the problem of the structure of Marvel's ketone may be considered to be definitely solved in favor of a spiroindan structure (VII), and therefore the cyclohydration of di-Δ^1-cyclohexenylacetylene takes place, for all other dienes, in accordane with a general scheme involving closing a five-membered ring:


(I)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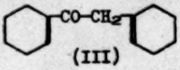
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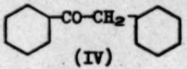
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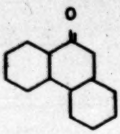
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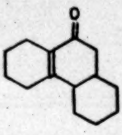
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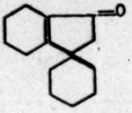
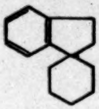
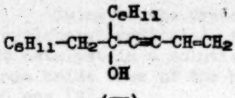

(VII)


(VIII)

Since di-Δ^1-cyclohexenylacetylene (II) is immediately converted into a cyclic ketone (VII) under Marvel's conditions (heating in a formic-acid solution), we felt it would be desirable to hydrate the dienyne (II), first to a dienone (III), and then to investigate the cyclization of this dienone and compare the cyclic ketone thereby synthesized with Marvel's ketone.

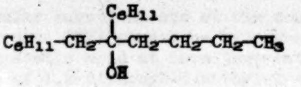
The dienyne (II) was prepared in the usual manner — by the dehydration of the acetylenic glycol (I) by potassium bisulfate. When the dienyne (II) is heated in a 90% methanol solution in the presence of sulfuric acid and mercuric sulfate, it is easily hydrated, like other dienynes, forming 1,2-di-(Δ^1-cyclohexenyl)-ethanone (III), with a yield of about 80%. When the dienyne (III) is hydrogenated in the presence of a Pt catalyst in a solution of glacial acetic acid or alcohol, two molecules of hydrogen are absorbed as required by the theory, and the cyclohexylhexahydrobenzyl ketone (IV) described in the literature is formed. As might have been expected, when the diene (III) is heated with phosphoric acid, it cyclizes almost quantitatively, forming the same mixture of cyclic ketones that is produced in the direct cyclohydration of the dienyne (II) by Marvel's method or by phosphoric acid. Thus, the same product, chiefly or exclusively a spiroindanone (VII), is formed in both the cyclohydration of the dienyne (II) and the cyclization of the dienone (III). As for the admixture of the second isomer, it is hard to make a definite statement about the latter's structure at the present time. It is possible that this second isomer, formed in small amounts during the cyclization of the dienyne (II), is not the spiroindanone (VII) but has some other structure.

As has been shown in previous communications from our laboratory [7], $\Delta^{8,9}$-tetrahydroindan-3-ones are easily converted into the corresponding indans under the action of phosphoric acid at a temperature of 170-190° with the simultaneous dehydrogenation of the six-membered ring and the reduction of the carbonyl group. We tried to utilize this reaction to transform the spiroindanone (VII) into the spiroindan (VIII) recently described by Bogert and his associates [5]. We were unable to effect this conversion, however, as the spiroindanone (VII) proved to be surprisingly stable, being recovered unchanged, with more or less tarring, when heated to temperatures of 160-200° with phosphoric acid. This also purified the product of traces of the second isomer, making it more homogeneous and yielding only one semicarbazole with a m.p. of 227°, which corresponds to a semicarbazone of a low-fusing isomer of Marvel's ketone with a m.p. of 39°.



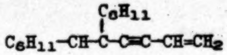
$$C_6H_{11}-CH_2-\overset{C_6H_{11}}{\underset{OH}{C}}-C\equiv C-CH=CH_2$$

(IX)



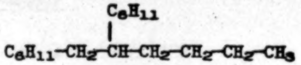
$$C_6H_{11}-CH_2-\overset{C_6H_{11}}{\underset{OH}{C}}-CH_2-CH_2-CH_2-CH_3$$

(X)



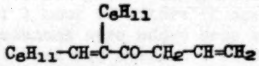
$$C_6H_{11}-CH-\overset{C_6H_{11}}{C}-C\equiv C-CH=CH_2$$

(XI)



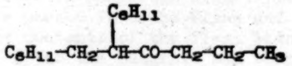
$$C_6H_{11}-CH_2-\overset{C_6H_{11}}{CH}-CH_2-CH_2-CH_2-CH_3$$

(XII)



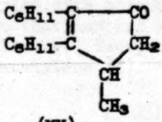
$$C_6H_{11}-CH=\overset{C_6H_{11}}{C}-CO-CH_2-CH=CH_2$$

(XIII)



$$C_6H_{11}-CH_2-\overset{C_6H_{11}}{CH}-CO-CH_2-CH_2-CH_3$$

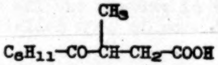
(XIV)



(XV)

$C_6H_{11}-COOH$

(XVI)



$$C_6H_{11}-CO-\overset{CH_3}{CH}-CH_2-COOH$$

(XVII)

Reacting vinylacetylenemagnesium bromide with the cyclohexylhexahydrobenzyl ketone (IV) synthesized cyclohexylhexahydrobenzylvinylethynylcarbinol (IX), with a yield of some 90%. The latter is also obtained with a yield of about 50% by condensing vinylacetylene with the ketone (IV) in the presence of powdered potassium hydroxide.

When the vinylacetylenic alcohol (IX) is hydrogenated with a Pt catalyst it absorbs three molecules of hydrogen and is transformed into butylcyclohexylhexahydrobenzylcarbinol (X). Dehydration of the vinylacetylenic alcohol (IX) by phosphoric acid yielded 5,6-dicyclohexyl-1,5-hexadien-3-yne (XI), which absorbs four molecules of hydrogen and is transformed into 1,2-dicyclohexylhexane (XII) when hydrogenated with a Pt catalyst in a solution of glacial acetic acid. When the dienyne (XI) is heated in aqueous solutions of methanol in the presence of sulfuric acid and mercury sulfate, 5,6-dicyclohexyl-1,5-hexadiene-4-one (XIII) is formed; when the latter is hydrogenated with a Pt catalyst, 5,6-dicyclohexylhexan-4-one (XIV) is formed.

Hydration of the dienyne (XI), like that of its phenyl analogue [8], is rather harder to accomplish than that of similar asymmetrical substituted dienynes with small aliphatic radicals, and therefore the reaction must be carried on for a longer time in these cases.

Under the action of phosphoric acid the dienone (XII) is smoothly cyclized, to 1,2-dicyclohexyl-3-methyl-1-cyclopenten-5-one (XV), the ozonization of which yields cyclohexanecarboxylic acid (XVI) and, apparently, the keto acid (XVII), which we were unable to obtain in the pure state, however.

Owing to the presence of two bulky substitutents at the double bond (cyclohexyl radicals), the cyclopentenone (XV) cannot be hydrogenated with a Pt catalyst in a solution of glacial acetic acid at room temperature. The same holds true of the hydrogenation of 1,2-diphenyl-3-methyl-1-cyclopenten-5-one [8].

EXPERIMENTAL

Synthesis of Dicyclohexylolacetylene

Into a round-bottomed three-necked flask there were poured 70 g of powdered potassium hydroxide and 1 liter of anhydrous ether. During the course of 1 hour 20 liters of acetylene were passed into the flask and 105 g of cyclohexanone were added drop by drop, the contents of the flask being constantly stirred and chilled with ice water. After the reagents had been added, the reaction mass was stirred for 2 hours at 0° and for 3 hours at room temperature, and then set aside to stand overnight. The next day the product was treated with water, extracted with ether, neutralized with 5% hydrochloric acid, dried with potash, and distilled in vacuo. This yielded 13 g of cyclohexanone that had not entered into the reaction, all the residue in the flask crystallizing. Recrystallization from benzene yielded 65 g of pure dicyclohexylolacetylene (I).

Dehydration of Dicyclohexylolacetylene

A carefully pulverized mixture of 170 g of the glycol (I) and 45 g of freshly calcined potassium bisulfate were placed in a Claisen flask. The mixture was heated for 1.5 hours to a temperature of 145-155° in a current of nitrogen, 25 ml of water being driven off. Then the raw carbon dioxide was driven off from the potassium bisulfate in a vacuum set up by a water-jet pump, and the flask contents were dried with sodium sulfate and re-distilled.

We obtained 110 g of di- Δ^1-cyclohexenylacetylene (II). The yield was 77%. B.p. 125-128° at 4 mm; n_D^{17} 1.5573.

Hydration of Di- Δ^1-Cyclohexenylacetylene

A mixture of 110 g of the dienyne (II), 330 g of 90% methanol, 1 ml of concentrated sulfuric acid, and 8 g of mercury sulfate was stirred energetically for 4.5 hours at a temperature of 60-65°. During the reaction process 21 g of additional mercury sulfate was added in 4 batches – 45 minutes apart. The product was diluted with water (100 ml), extracted with ether, neutralized with soda, dried with sodium sulfate, and fractionated in vacuo. Yield: 98 g of 1,2-di-(Δ^1-dicyclohexenyl)-ethanone (III).

B.p. 128-130 at 4 mm; n_D^{20} 1.5247; d_4^{20} 1.0071; MR found 62.04; calculated 61.53.

6.295 mg substance: 18.862 mg CO_2; 5.502 mg H_2O.
6.510 mg substance: 19.504 mg CO_2; 5.675 mg H_2O.
Found %: C 81.77, 81.76; H 9.78, 9.75.
$C_{14}H_{20}O$. Calculated %: C 82.35; H 9.80.

1,2-Di(Δ^1-cyclohexenyl)-ethanone is a light-yellow mobile liquid with a specific odor. It rapidly oxidizes when exposed to the air, with a change in its refractive index, which explains the lowered per cent of carbon found upon analysis. 1,2-Di-(Δ^1-cyclohexenyl)-ethanone easily yields a semicarbazone, which attains a stable m.p. of 172-173° after a preliminary recrystallization from methanol.

3.47 mg substance: 0.495 ml N_2 (22°, 740 mm).
3.30 mg substance: 0.485 ml N_2 (22°, 740 mm).
Found %: N 16.07, 16.26.
$C_{15}H_{23}ON_3$. Calculated %: N 16.09.

Hydrogenation of 1,2-Di-(Δ^1-cyclohexenyl)-ethanone

160 g of the freshly distilled dienyne (III) were dissolved in 160 ml of ethanol and hydrogenated in the presence of a Pt catalyst prepared by the Adams method. At first, hydrogenation was very violent, but it slowed down toward the end, lasting 30 hours all told. 40 liters of hydrogen were absorbed, whereas the hydrogenation of two double bonds should have required 40.9 liters of hydrogen according to theory. Repeated careful fractionations of the product in vacuo yielded 130 g of cyclohexylhexahydrobenzyl ketone (IV), a light yellow liquid:

B.p. 110-112° at 4 mm; n_D^{20} 1.4840; d_4^{20} 0.9500;
MR found 62.63; calculated 62.46.

The semicarbazone of cyclohexylhexahydrobenzyl ketone fused at 186-187° after recrystallization from methanol.

4.27 mg substance: 0.588 ml N_2 (23°, 743 mm).
3.63 mg substance: 0.506 ml N_2 (23°, 743 mm).
Found %: N 15.53, 15.72.
$C_{15}H_{27}ON_3$. Calculated %: N 15.85.

The oxime of cyclohexylhexahydrobenzyl ketone fused at 114° after recrystallization from methanol.

5.21 mg substance: 6.279 ml N_2 (22°, 752 mm).
6.27 mg substance: 6.338 ml N_2 (22°, 755 mm).
Found %: N 6.11, 6.20.
$C_{14}H_{20}ON$. Calculated %: N 6.27.

The same results were obtained by hydrogenating the dienone (III) in a solution of glacial acetic acid.

According to the literature, the constants of cyclohexylhexahydrobenzyl ketone are as follows:

B.p. 159-162° at 12 mm; d_4^{20} 0.9511; semicarbazone m.p. 190-191°;
oxime m.p. 112-113°, [9].

Cyclization of 1,2-Di-(Δ^1-cyclohexenyl)-ethanone

5 g of the dienone (III) and 5 ml of phosphoric acid (sp. gr. 1.77) were mixed together for 6 hours at a temperature of 60°. The reaction product was diluted with water, extracted with ether, neutralized with a soda solution,

dried with sodium sulfate, and fractionated in vacuo. Yield: 3.8 g of the cyclic ketone (VII):

B.p. 120-121° at 3 mm; n_D^{17} 1.5293.

Its semicarbazone fused at 218° (from methanol) and caused no depression when mixed with the semicarbazone synthesized from Marvel's cyclic ketones (vide infra). At a temperature of 15° cyclization of the dienone (III) by phosphoric acid is highly incomplete, almost all the dienone being recovered unchanged (melting point of the semicarbazone and mixed test sample: 172-173°). The cyclization of the dienone (III) with phosphoric acid is incomplete even after 15 hours at 30°, the end product being the cyclic ketone (VII), contaminated with the initial dienone.

Cyclohydration of Di-Δ^1-cyclohexenylacetylene

28 g of the dienyne (II) and 280 g of formic acid (sp. gr. 1.21) were vigorously stirred together for 10 hours at 55-60°. The formic acid was driven off in a slight vacuum at 55-60°. The residue was diluted with water, extracted with ether, neutralized with a soda solution, dried with sodium sulfate, and fractionated. Yield: 21.5 g of the cyclic ketones described by Marvel:

B.p. 116-119° at 2 mm; n_D^{17} 1.5295.

Their semicarbazone fused at 218-219° (from methanol) and caused no depression when mixed with the semicarbazone of the cyclic ketone (VII) described above and synthesized by cyclization of the dienone (III).

Phosphoric-Acid Treatment of the Product of Cyclohydration of Di-Δ^1-cyclohexenylacetylene

A mixture of 20 ml of crystalline phosphoric acid (sp.gr. 1.86 at 40°) and 22 g of the cyclic ketones produced by the Marvel cyclohydration of the dienyne (II) by formic acid as described above was stirred for 3 hours at a temperature of 150°. The product was diluted with water, extracted with ether, neutralized with soda, dried with sodium sulfate, and fractionated. Yield: 12 g of the purified cyclic ketone (VII):

B.p. 144-146° at 4 mm; n_D^{20} 1.5391.

The semicarbazone of this ketone fused at 226-227° (from methanol), which corresponds to the semicarbazone of the low-fusing cyclic ketone (VII) with a m.p. of 39° isolated by Linstead and Walpole from Marvel's ketones [4].

Synthesis of Cyclohexylhexahydrobenzylvinylethynylcarbinol by the Condensation of Vinylacetylene with Cyclohexylhexahydrobenzyl ketone

In a round-bottomed flask, fitted with a stirrer, there were placed 45 ml of anhydrous ether and 13 g of powdered potassium hydroxide. A mixture of 13 g of cyclohexylhexahydrobenzyl ketone (IV), 11 g of vinyl-acetylene, and 10 ml of sulfuric ether was added over the course of 15 minutes while the flask was chilled with ice water and its contents were vigorously stirred. The next reaction mass was stirred for 1 hour while chilled and for 8 hours at room temperature. The next day the product was carefully treated with water (15 ml), extracted with ether, neutralized with 5% hydrochloric acid, dried with sodium sulfate, and fractionated in vacuo. We recovered 2 g of the unreacted ketone (IV) and 9 g of cyclohexylhexahydrobenzyl-vinylethynylcarbinol (IX) as a colorless, extremely viscous liquid with a specific odor:

B.p. 157-159° at 4 mm: n_D^{20} 1.5167; d_4^{20} 0.9791;
MR found 80.29; calculated 79.98.

6.465 mg substance: 19.686 mg CO_2; 6.240 mg H_2O.
3.137 mg substance: 9.585 mg CO_2; 2.979 mg H_2O.
Found %: C 83.10, 83.47; H 10.80, 10.63.
$C_{18}H_{28}O$. Calculated %: C 83.08; H 10.85.

Synthesis of Cyclohexylhexahydrobenzylvinylethynylcarbinol by the Grignard Method

To vinylacetylenemagnesium bromide prepared in the usual manner (10.9 g of magnesium, 230 ml of absolute ether, 55 g of ethyl bromide, and 48 g of vinyl acetylene) there were added during 40 minutes at room temperature 57 g of cyclohexylhexahydrobenzyl ketone (IV) dissolved in 80 ml of absolute ether. Five to ten minutes after the ketone had been added, a magnesium organic complex was precipitated, and the reaction mass was diluted with 200 ml of absolute ether, after which it was stirred for 12 hours at 35°. The next day the product was hydrolyzed with 8% hydrochloric acid (250 ml), extracted with ether, dried with sodium sulfate, and fractionated in small batches (10-15 g) in vacuo in the presence of pyrogallol. The sole product isolated was 58 g of the cyclohexylhexahydrobenzylvinylethnyl-carbinol (IX) described above:

B.p. 155-157° at 4 mm; n_D^{20} 1.5180.

Hydrogenation of Cyclohexylhexahydrobenzylvinylethynylcarbinol

2.7 g of the carbinol (IX) were hydrogenated in a solution of 25 ml of methanol in the presence of a Pt catalyst prepared by the Adams method. Reduction of one double and one triple bond should require the absorption of 770 ml of hydrogen. Actually 800 ml were absorbed. Yield: 2 g of butylcyclohexylhexahydrobenzylcarbinol (X):

B.p. 129-133° at 2 mm; n_D^{20} 1.4920; d_4^{20} 0.9471;
MR found: 81.43; calculated: 82.45.

5.690 mg substance; 16.946 mg CO_2; 6.352 mg H_2O.
6.959 mg substance: 20.079 mg CO_2; 7.548 mg H_2O.
Found %: C 81.30, 81.07; H 12.50, 12.47.
$C_{18}H_{34}O$. Calculated %· C 81.20; H 12.78.

Dehydration of Cyclohexylhexahydrobenzylvinylethynylcarbinol

8 g of the carbinol (IX) and 8 ml of phosphoric acid (sp. gr. 1.76) were energetically stirred together for 5 hours at 50-65°. The product was diluted with ether, neutralized with a soda solution, dried with sodium sulfate, and fractionated in vacuo. Yield: 3.5 g of 5,6-dicyclohexyl-1,3-hexadien-3-yne (XI),

a yellowish, very viscous fluid:

B.p. 135-137° at 4 mm; 124-126° at 2.5 mm; n_D^{20} 1.5310;
d_4^{20} 0.9331; MR found 80.22; MR calculated: 77.99.

5.140 mg substance: 16.722 mg CO_2; 5.025 mg H_2O.
Found %: C 88.78; H 10.94.
$C_{18}H_{28}$. Calculated %; C 89.18; H 10.82.

Dehydration of the carbinol (IX) by 60% sulfuric acid under the same conditions yields similar results. We were unable to dehydrate the carbinol (IX) with potassium bisulfate.

Hydrogenation of 5,6-Di-cyclohexyl-1,5-hexadien-3-yne

1.1 g of the dienyne (XI) was dissolved in 12 ml of glacial acetic acid and hydrogenated in the presence of a Pt catalyst prepared by the Adams method. Reduction of two double bonds and one triple bond should require 450 ml of hydrogen; actually 500 ml of hydrogen were absorbed. The hydrogenation product is deposited out of a solution of glacial acetic acid, and some ether was added before neutralization to keep it in solution. Then a 30% solution of an aqueous alkali was added to the solution drop by drop, with stirring and chilling, until all the acetic acid was neutralized. The product was extracted with ether, dried with sodium sulfate, and fractionated. The yield was 1 g of 1,2-dicyclohexylhexane (XII) as a rather mobile liquid:

B.p. 111-113° at 2 mm; n_D^{20} 1.4850; d_4^{20} 0.8917;
MR found: 80.35; calculated 80.94.

4.725 mg substance: 14.904 mg CO_2; 5.580 mg H_2O.
3.948 mg substance: 12.499 mg CO_2; 4.846 mg H_2O.
Found %: C 86.08, 86.40; H 13.21, 13.74.
$C_{18}H_{34}$. Calculated %: C 86.40; H 13.60.

Hydration of 5,6-Dicyclohexyl-1,5-hexadien-3-yne

13 g of the dienyne (XI), 55 g of 90% methanol, 0.33 ml of sulfuric acid, (sp.gr.1.83), and 5 g of mercuric sulfate were energetically stirred for 15 hours at 60-65°. During the reaction process another 10 g of mercury sulfate was added every two hours in 1.5-2 g batches. The product was extracted with ether, neutralized with water, dried with sodium sulfate, and fractionated in vacuo. Yield: 6 g of 5,6 dicyclohexyl-1,5-hexadien 4-one (XIII), a rather mobile yellow liquid that rapidly oxidizes in the open air and has a specific odor:

B.p. 143-145° at 3 mm; n_D^{20} 1.5042; d_4^{20} 0.9613;
MR found 80.12; calculated 80.00.

11.10 mg substance: 33.01 mg CO_2; 10.98 mg H_2O.
8.22 mg substance: 24.45 mg CO_2; 8.15 mg H_2O.
Found %: C 81.16, 81.18; H 11.07, 11.09.
$C_{18}H_{28}O$. Calculated %: C 83.08; H 10.85.

We were unable to perform an analysis of the dienone that would be closer to the theory, apparently owing to its oxidation in the air.

The 2,4-dinitrophenylhydrazone of this dienone fused at 60-65° (from methanol).

3.530 mg substance: 0.407 ml N_2 (25°, 745 mm).
Found %: N 12.95.
$C_{24}H_{32}O_4N_4$. Calculated %: N 12.72.

Hydrogenation of 5,6-Dicyclohexyl-1,5-hexadien-4-one

2 g of the dienone (XIII) was dissolved in 15 ml of glacial acetic acid and hydrogenated in the presence of a Pt catalyst prepared by the Adams method. In the space of 40 minutes 210 ml of hydrogen were absorbed, after which the process of hydrogenation slowed down considerably. Calculation indicates that the reduction of two double bonds requires 380 ml of hydrogen. After neutralization of the acetic acid with a 30% alkali, the product was extracted with ether, dried, and fractionated. Yield: 1.5 g of 5,6-dicyclohexylhexan-4-one (XIV).

B.p. 122-124° at 3 mm; n_D^{20} 1.4912; d_4^{20} 0.9559;
MR found 79.41; calculated 80.47.

4.210 mg substance: 12.337 mg CO_2; 4.367 mg H_2O.
Found %: C 79.97; H 11.60.
$C_{18}H_{32}O$. Calculated %: C 81.81; H 12.12.

We were unable to synthesize crystalline derivatives of 5,6-dicyclohexylhexan-4-one.

Cyclization of 5,6-dicyclohexylhexadien-4-one

5 g of the dienone (XIII) and 5 ml of phosphoric acid (sp.gr. 1.81) were vigorously stirred together for 5 hours at 70-75°. The product was diluted with water, extracted with ether, neutralized with soda, dried with sodium sulfate and fractionated in vacuo. Yield: 2.5 g of 1,2-dicyclohexyl-3-methyl-1 cyclopenten-5-one (XV), a very viscous, light-yellow liquid with an agreeable odor:

B.p. 142-143° at 2.5 mm; n_D^{20} 1.5225; d_4^{20} 0.9973;
MR found 79.70, calculated 78.27.

4.390 mg substance: 13.374 mg CO_2; 4.270 mg H_2O.
4.980 mg substance: 15.184 mg CO_2; 4.855 mg H_2O.
Found %: C 83.14, 83.21; H 10.88, 10.91.
$C_{18}H_{28}O$. Calculated %: C 83.08; H 10.85.

We were unable to synthesize the semicarbazone of this cyclic ketone, but with dinitrophenylhydrazine it yielded two isomeric 2,4 dinitrophenylhydrazones, which melted at 136-137° and 199° (from methanol).

The low-fusing, 2,4-dinitrophenylhydrazone (m.p. 136-137°) is a fine, free-flowing powder, which dissolves very easily in methanol in the cold:

3.430 mg substance: 0.382 ml N_2 (27°, 751 mm)
3.220 mg substance: 0.361 ml N_2 (27°, 748 mm)
Found %: N 12.52, 12.56.
$C_{24}H_{32}O_4N_4$. Calculated %: N 12.72.

The high-fusing 2,4-dinitrophenylhydrazone (m.p. 199°) is a powder that dissolves in methanol with great difficulty upon boiling.

3.750 mg substance: 0.423 ml N_2 (24°, 744 mm).
found %: N 12.69.
$C_{24}H_{32}O_4N_4$. Calculated %: N 12.72.

The synthesized cyclopentenone (XV) cannot be hydrogenated in a solution of glacial acetic acid at room temperature in the presence of a Pt catalyst. No hydrogen was absorbed during 18 hours of agitation in an atmosphere of hydrogen, the product remaining unchanged. We were unable to synthesize the cyclopentenone (XV) by cyclohydration of the dienyne (XI). The initial product was recovered unchanged after six hours of heating the dienyne to 70° with an equal volume of phosphoric acid (sp. gr. 1.81).

Ozonization of 1,2-Dicyclohexyl-3-methyl-1-cyclopenten-5-one

Ozonized oxygen was passed through a solution of 3.6 g of the cyclopentenone (XV) in 35 ml of chloroform for 6 hours at a rate of 5 liters per hour (ozone concentration: 6%).

The ozonide was decomposed by vigorous shaking with 45 ml of water for 5 hours at room temperature and for 16 hours at 60-65°. The product was neutralized with water, the chloroform was driven off, and the aqueous layer was extracted with ether. After the ether and chloroform had been driven off, the end product was 3.4 g of a substance exhibiting an acid reaction, which was treated three times with a 10% soda solution (30 ml at a time), with vigorous stirring and heating (55-60°). After this treatment the residue of neutral products weighed about 1 g; when it was distilled, we recovered 0.4 g of a substance (b.p. 167-170° at 2 mm; n_D^{24} 1.5080), which was not investigated further.

About 3 g of oily acids were isolated from the soda solution after evaporation, acidulation, and careful extraction with ether; 0.5 g of cyclohexanecarboxylic acid (XVI) (b.p. 130-139° at 2 mm; n_D^{20} 1.4540), was distilled from these acids in an oil-pump vacuum. Acid (XVI) crystallized upon cooling in characteristic transparent crystals that fused at 21-22°.

13.04 mg substance; 10.18 ml 0.01 N NaOH
11.90 mg substance: 9.54 ml 0.01 N NaOH.
Found M: 128, 125.
$C_7H_{12}O_2$. Calculated M: 128.

Analysis of the silver salt of cyclohexanecarboxylic acid yielded the following results:

0.0625 g substance: 0.0287 g Ag.
0.1084 g substance: 0.04938 g Ag.
Found %: Ag 45.92, 45.48.
$C_7H_{11}O_2Ag$. Calculated %: Ag 45.95.

The residue left behind when the cyclohexanecarboxylic acid was driven off was distilled in a high vacuum from a small flask with a low outlet tube. This yielded about 1 g of a thick oil (b.p. 179-184° at 0.06 mm; n_D^{28} 1.4830), which partly crystallized. At first the crystals fused at 148-152°, but after repeated washing with ether they fused at 162°; it is possible that they are a keto acid (XVI). We were unable to synthesize its semicarbazone or dinitrophenylhydrazone, however, nor were we able to obtain satisfactory analytical data. Per cent found: C 63.52; H 8.72, instead of C 66.66; H 9.09.

SUMMARY

Hydration of di-Δ^1-cyclohexenylacetylene (II) in aqueous solutions of methanol in the presence of sulfuric acid and mercury sulfate produces a high yield of di-Δ^1-cyclohexenylethanone (III), which is converted into cyclohexylhexahydrobenzyl ketone (IV) by hydrogenation with a Pt catalyst. Cyclization of the dienone (III) with phosphoric acid forms spiroindanone (VII), which is identical with Marvel's ketone synthesized directly by the cyclohydration of the dienyne (II).

Condensation of vinylacetylene with cyclohexylhexahydrobenzyl ketone (IV) produces a high yield of cyclohexylhexahydrobenzylvinylethynylcarbinol (IX), which is hydrogenated with a Pt catalyst to the corresponding saturated carbinol (X) and dehydrated to the dienyne (XI). When the latter is hydrogenated with a Pt catalyst, it absorbs the 4 molecules of hydrogen required by theory and is converted into 5,6-dicyclohexylhexane (XII). Hydration of the dienyne (XI) in aqueous solutions of methanol yield the dienone (XIII), which is cyclized smoothly to the cyclopentenone (XV) by phosphoric acid, as are other analogous dienynes.

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